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GÖSTA R. ANDERSSON

A study of the pressure dependence of the partial specific volume of macromolecules in solution by compression measurements in the range 1–8000 atm

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A study of the pressure dependence of the partial specific volume of macromolecules in solution by compression measurements in the range 1–3000 atm

By GÖSTA R. ANDERSSON

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Preface

The investigation described in this paper has been carried out at the Institute of Physical Chemistry of the University of Uppsala during the years 1959–1962.

I wish to express my sincere gratitude to the head of the Institute, Professor Stig Claesson, for suggesting this work and for his continuous interest, encouragement and helpful advice in day-to-day discussions and for placing the greatest possible facilities at my disposal.

I should also like to extend my warmest thanks to colleagues and friends at the Institute for aid during this work, particularly Drs. Lars-Olof Sundelöf and Anders Mård for their stimulating discussions and valuable suggestions and Mr. Evald Hellman and his coworkers for help with numerical calculations.

The English text has been revised by Dr. Phil G. Squire and I thank him for his many suggestions.

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Uppsala, January 1963.

Introduction

In recent years the partial specific volume of macromolecules in solution at high pressures has attracted increasing interest, due mainly to its importance in accurate work in ultracentrifugation. Although an experimental procedure was evolved in the early nineteen-thirties by Adams [1] for determining the partial specific volume of low molecular weight substances at high pressures (up to 12,000 bars), little has been done in this field as regards macromolecules in solution. The main purpose of this investigation has therefore been to obtain experimental data not previously available for these polymer substances.

The partial specific volume of a substance is a quantity derived from the volume of a solution and the concentration of the substance in that solution. Quite naturally, therefore, its experimental determination is in general based on a determination of the interrelated values of these two quantities, as each of these is relatively easy to obtain experimentally. The density of a solution is often measured instead of its volume, using for this purpose pycnometer methods and float methods. Of the latter, the magnetic float method is especially accurate but is tedious in practice.

At atmospheric pressure it is often possible to choose one of a variety of different methods for measuring the density depending upon, for instance, the accuracy

which is desired. At high pressures, however, this possibility is limited owing to technical reasons, which exclude the use of the above-mentioned magnetic float method. Hitherto, however, no attempt seems to have been made to use the same apparatus for density measurements at high pressures as is used at atmospheric pressure, although this would obviously lead to an increased accuracy for the determination of the change of the partial specific volume with pressure, provided the apparatus gives accurate results at all pressures. With the pycnometer method, or rather the piezometer method, introduced in the present investigation, density measurements can be made with the same apparatus at 1 atm and at high pressures with standard deviations amounting to $\pm 4 \cdot 10^{-5}$ g/ml and $\pm 7 \cdot 10^{-5}$ g/ml respectively, corresponding to ± 0.003 ml/g and ± 0.006 ml/g in the determination of the partial specific volume of the macromolecules. Another feature of the experimental procedure adopted which also promotes high accuracy is the simultaneous subjection to high pressure of many piezometers containing macromolecular solutions of different concentrations. The latter technique also has the advantage that it does not require a high accuracy in the pressure determination and it is very time-saving in comparison with earlier high pressure experiments of similar type.

Chapter 1. High pressure apparatus

a. *Pressure vessel and packings*

The high pressure apparatus is of conventional design (Fig. 1), but modified in such a way that the pressure chamber is formed by a hole passing through the entire cylinder, equipped at both ends with tightly fitting pistons. A detailed account of the high pressure apparatus will be published by Claesson and Mård [2]. The hole passing straight through the cylinder is important, as it facilitates the removal of the pistons without the need for special tools, and in the rare cases when the upper piston had cut into the cylinder wall, this feature proved to be very advantageous. The outer and inner diameters of the pressure vessel are 260 mm and 76.6 mm respectively, and its length is 270 mm. The pressure vessel is filled with a liquid and the pressure is generated by forcing piston B (Fig. 1) into the cylinder by a hydraulic press D. The capacity of the press is 500 metric tons. The liquid is prevented from leaking by a packing C at each end of the bore. The pressure range used was 675–8200 atm, which permitted the use of very simple packings. To get as large a volume as possible under pressure, glycerol was used as a pressure medium, since it is one of the least compressible of all non-metallic liquids. By this means the highest pressure, 8200 atm, could be obtained in a volume as large as 600 ml.

The most commonly used packing in the experiments was Poulter's [3] packing. This simple and effective packing, consisting of a tightly fitting rubber bung, could be used up to 6000 atm before it started to leak. The frictional forces in the packings in the pressure vessel and in the hydraulic press were in general so constant that a rough measure of the pressure inside the vessel could be obtained from readings on the Bourdon gauge on the hydraulic press. The maximum pressure in the pressure vessel was determined by an indirect method, which will be described later. One of the major advantages of Poulter's packing is the ease with which it can be removed from the bore, using a simple hook forced between the cylinder wall and the bung. In the higher pressure regions a piston with three O-ring packings was used. The piston was of a new design described by Malmrud and Andersson [4]. The piston

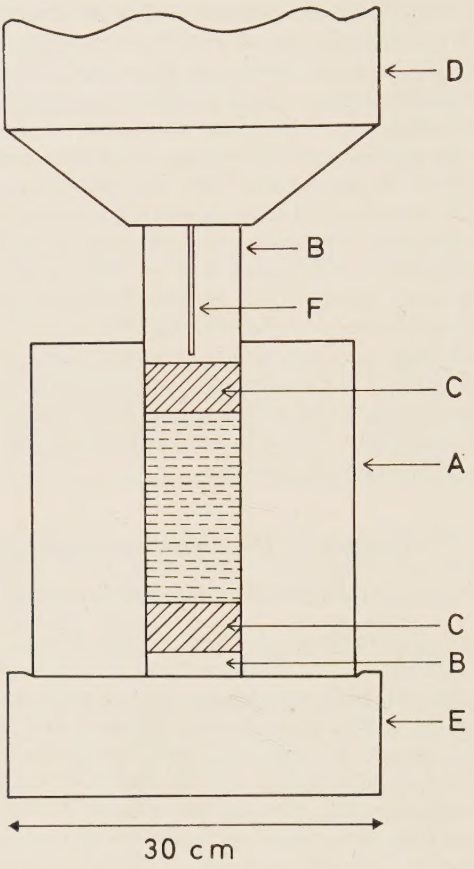

Fig. 1. Sketch of high pressure apparatus. A, pressure vessel; B, pistons; C, packings; D, hydraulic press; E, press platen; F, hole for thermocouple.

is constructed of nylon, which in this case has proved to have better mechanical properties than steel. With the same thickness of supporting material between the O-ring grooves, the nylon piston could stand a much higher pressure than the steel piston. According to Lawson [5] the pressure in the pressure vessel is sustained by the successive pressure barriers, which from the inside and out are built up between adjacent O-rings by small amounts of liquid which manage to leak past the O-rings. This implies that there should be a sudden drop in pressure when the liquid leaks past an O-ring. This assumption is supported by the fact that when the outermost O-ring leaks a sudden decrease of the compressive force of the hydraulic press can be registered. The sudden leak sometimes caused trouble at the highest pressures, so that some experiments had to be repeated. When the Poulter's packings leaked no rapid fall of the pressure could be noticed.

The pressure vessel was kept at room temperature ($21.5° \pm 3°C$) during most of the determinations, and although drifts in temperature were noted over an extended period, short term fluctuations were negligible due to the large mass of the system.

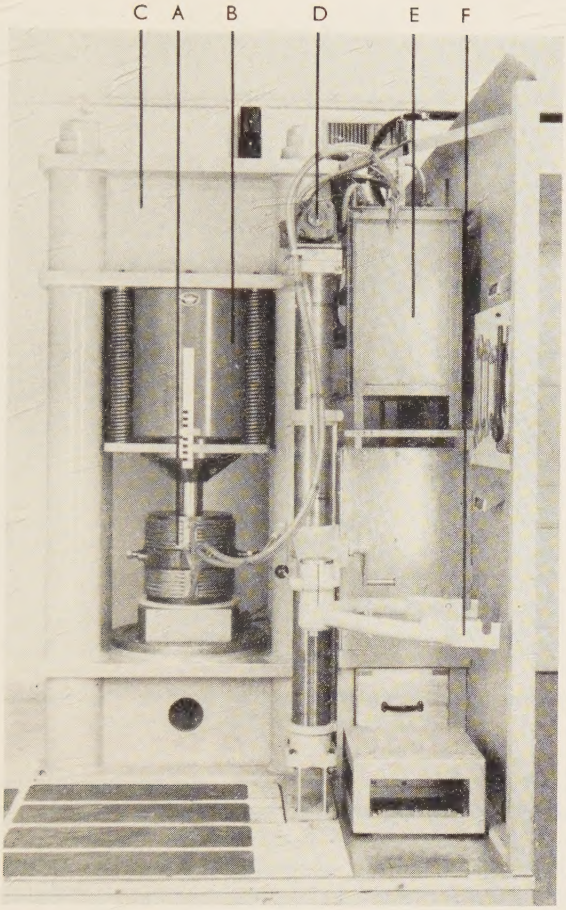

Fig. 2. High pressure apparatus. A, pressure vessel with water jacket; B, hydraulic press; C, frame; D, pump; E, thermostat; F, fork for lifting the pressure vessel.

In cases where experiments were made at temperatures considerably removed from room temperature, constant temperature was achieved by pumping water from a thermostat, E in Fig. 2, through copper tubes which were in good thermal contact with the vessel A. To isolate the vessel from thermal contact with the press platen an 11 mm thick sheet of eternite[1] was placed between them. The temperature fluctuations inside the pressure vessel were ± 0.05°C at 1 atm. On increasing or decreasing the pressure the temperature in the vessel changed, owing to the pressure-volume work, by several tenths of a degree; this could be registered by means of a thermocouple with one joint situated at the bottom of a narrow hole in the top piston (F in Fig. 1).

b. *Description of the piezometers used*

The volume change of the polymer solution at high pressures was measured in a new type of piezometer, which is shown diagrammatically in Fig. 3. It consists of a

[1] A commercial preparation of asbestos reinforced with cement.

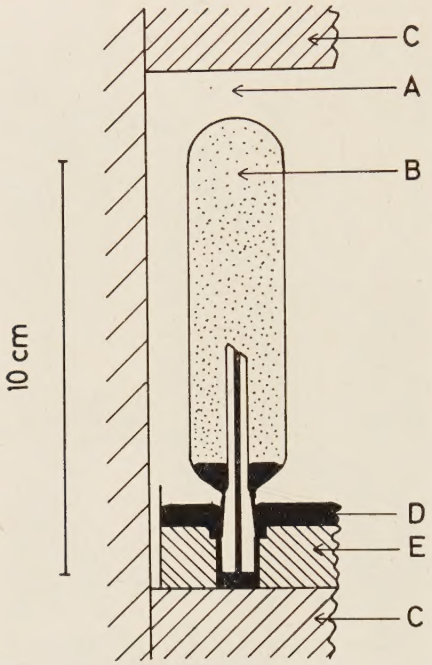

Fig. 3. One of the piezometers in the pressure vessel. A, glycerol; B, solution; C, piston; D, mercury; E, Teflon.

flask of Pyrex glass 7740 with a ground glass stopper through which passes a capillary tube. The piezometer containing the polymer solution is immersed in the pressure-transmitting liquid in the pressure vessel. The stopper with the capillary tube dips into mercury, which is held in a container. When the pressure is increased the liquid contracts and mercury flows through the capillary tube and collects inside the piezometer. Upon releasing the pressure the liquid expands and a part of it flows out through the capillary tube, but the mercury inside the piezometer is trapped. The volume of the trapped mercury is a measure of the volume decrease of the compressed liquid at the maximum pressure during the experiment.

Glass piezometers have often been used for the determination of the volume change of liquids under high pressure. Bridgman [6] was doubtful about their reliability at higher pressures because of hysteresis and other irregular effects he had observed with glass at 6000 atm. Adams [1], however, reports very consistent results obtained from compression measurements with glass piezometers. Gibson [7] further justifies their use and as a comparison he has determined the compression of water both with a piezometer of Pyrex glass and with one of vitreous silica at 1000 bars. The results were 0.03935 ± 0.00005 and 0.03930 ± 0.00004 respectively, thus showing agreement within the limits of the experimental errors. Gibson [8] also points out that inconsistent results obtained with glass piezometers can partly be ascribed to strains in the glass. Strained glass behaves anisotropically under pressure thus causing anomalous changes in the piezometer volume. A careful heat pretreatment of the piezometers to lessen the strain in the glass is therefore important. If piezometers of

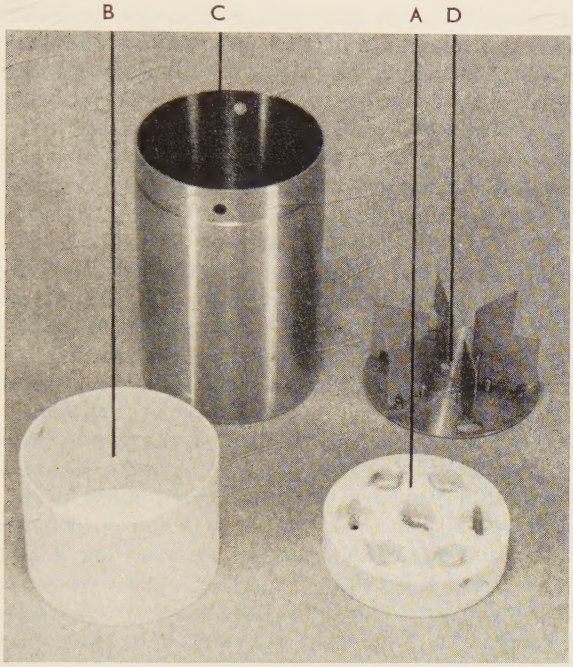

Fig. 4. Photograph of holder. A and B, for seven piezometers together with steel capsule C and cover with radially arranged plates D.

simple construction, as used in the present investigation are employed, however, there are few places where such strains can arise.

In the present investigation the piezometers were heated to 550° C in an electric furnace. They were kept at this temperature for an hour and were then allowed to cool as rapidly as the furnace, which was about 1° per minute during the first 90 minutes. Before being calibrated the piezometers were subjected to high pressure three or four times in the hope that possible, remaining defects would thereby be exposed. Finally the volumes of the piezometers were determined by the common procedure of weighing them with air-free, distilled water. In the separate determination of the volumes of the capillaries, mercury was used instead of water. The densities necessary for these volume determinations were taken from works by Dorsey [9] and Beattie *et al.* [10].

The piezometers used have volumes which are about twice or three times as large as those of the piezometers described by Gibson [8] and Adams [1]. The volumes varied between 22 and 26 ml. The amount of mercury which flows into the piezometer depends on the pressure and the compressibility of the liquid. When the piezometers have contained water the volume of trapped mercury has varied from 0.5 ml to 3.5 ml in the pressure region 675–8200 atm. In other cases the volume has been larger, as water is one of the least compressible liquids. Piezometers with stoppers of different lengths were used during the investigation. A total length of 55 mm, of which 30 mm is inside the bulb, proved to be the most convenient. Longer stoppers are

easily broken on removal from the piezometers. The volume of the stem ought to be so large that not all the mercury in it is driven out by a minor pressure decrease outside the piezometer. The capillary tubes of the above-mentioned stoppers have a volume of about 0.035 ml, which implies that for water solutions at low pressures a pressure drop of some 30 atm is permissible without any liquid in the piezometer flowing out through the capillary. The inner end of the stopper is obliquely ground to facilitate the falling of the mercury drops. The piezometer of this description can naturally also be used as a pycnometer. In this investigation it was used as such at 1 atm to determine the density of polymer solutions and then in the inverted position to measure the volume decrease of the same polymer solutions at high pressures. One advantage with the type of piezometer described, with a capillary through the stopper, is that the liquid in it can be brought to temperature equilibrium in a water thermostat without the liquid in the stem coming in contact with the water.

A special holder for seven piezometers was made of Teflon, A and B in Fig. 4, and constructed so that A fits into B. It also functioned as a container for the mercury, which had to be present in considerable amounts as a volume contraction of three or four millilitres for each solution was common at pressures around 4500 atm. In order to protect the piezometers from damage in the pressure vessel they were placed in a stainless steel capsule C; the capsule cover D is equipped with radially arranged plates, which hold the piezometers in a vertical position. The height of the capsule is adjusted so that the distance between the cover and the piezometers is not more than one millimeter, thereby preventing the piezometers from floating in the pressure-transmitting liquid, glycerol. The cover is attached to the capsule by means of a clamp. Due to the buoyancy of glycerol it proved to be convenient to fill the capsule containing the piezometers with glycerol only after the cover had been attached to the capsule.

Chapter 2. Materials and their properties

a. *Purity of materials and preparation of solutions*

The compression measurements (see Chapter 4) have revealed that the concentration dependence of the compression does not vary by more than approximately a factor of ten when different polymers are used as solutes. The largest variation occurs for polyelectrolytes, where the variation is approximately the same as for electrolytes. Fluctuations of trace amounts of impurities in the polymers used will therefore not lead to very irregular results for the compression measurements.

The partial and apparent specific volumes at 1 atm do not seem to be very sensitive to impurities of the solvent either. The present author agrees with a statement by Jessup [11] that "it seems very improbable that the purity of the solvent has any appreciable effect on the values of apparent specific volume derived from measurements of densities of solvents and solution". As a rule, therefore, the solvents were not subjected to further purification by distillation before use. The determination of the density of the solvent used at 1 atm, which was a part of every compression measurement, ensured that the solvent was of adequate purity (see p. 525).

The solutions to be investigated were made up directly, by dissolving the polymer in the solvent, or by diluting a previously prepared stock solution. The solutions were prepared on the basis of weight of polymer per weight of solvent. For the following eight substances: dextran, hydroxyethyl cellulose, polyethylene glycol (the high molecular weight fraction), polymethacrylic acid, polyvinyl alchohol, sodium

carboxymethyl cellulose, nitrocellulose and glucose, stock solutions were prepared and their concentrations were determined; for the first six water solutions by freeze-drying samples of the stock solutions and for the remaining two by direct weighing. The reproducibility of the concentration determinations by freeze-drying was checked and the deviation between subsequent determinations was about ± 0.1 %.

In addition to distilled water, the following solvents were used for the high pressure experiments or for the viscosity measurements. The origin and degree of purity are also recorded.

Acetone, AB. Svenska Shell, puriss.
n-Amyl alcohol, Eastman Kodak Company, practical
Cadoxen, the preparation of the solvent is given by Henley [12]
Chlorobenzene, Grave AB., puriss.
Chloroform, Grave AB., puriss.
Cyclohexane, Eastman Kodak Company, practical
Cyclohexanone, Riedel-E. de Haën AG., rein and Kebo AB., purum
Ethanol, AB. Vin- och Spritcentralen, 99.5 % by volume
Ethyl acetate, Merck, p.a. für Chromatografie
Formic acid 98–100 %, Merck, p.a.
Methanol, Merck, p.a. für Chromatografie and Grave AB., purum
Methyl ethyl ketone, Grave AB., purum
Methyl isobutyl ketone, Grave AB., purum
n-Octane, Fluka AG., purum
sym-Tetrachloroethane, Kebo AB., puriss.
Toluene, J. T. Baker Chemical Company, analyzed A.C.S.
m-Xylene, Kebo AB., puriss.

Information about the macromolecular substances used is given in Chapter 6, together with particulars about the preparation of solutions.

b. *Molecular weight determinations*

During the course of the investigation it was established that the molecular weight of the polymers had no influence on the pressure dependence of the partial specific volume (see p. 554). The extensive work which accompanies an accurate determination of the molecular weight was therefore not undertaken, but the average molecular weight of the polymers was determined viscosimetrically. For the same reason, and also owing to the large amount of polymer needed for each experiment, no fractionation of the different substances was attempted.

The intrinsic viscosities of the different polymers, dissolved in appropriate solvents, were determined in standard capillary viscometers of the Ubbelohde type available at this Institute. For each polymer-solvent system, the viscosity was measured at five different concentrations, so chosen that the relative viscosity of the highest concentration did not exceed approximately 2.2. As the purpose of the molecular weight determinations was to give the right order of magnitude of the molecular weights, the small kinetic energy correction term was discounted in the viscosity measurements. For the same reason the rate of shear dependence of the viscosity was generally neglected, as this effect is also small in solutions of nonpolyelectrolytes in the molecular weight range up to 1,000,000, and does not introduce an error of

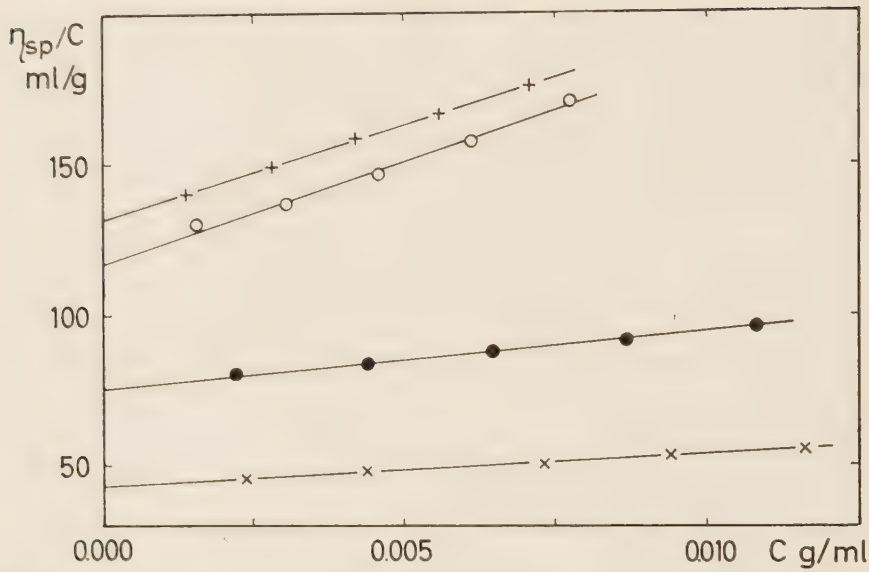

Fig. 5. A plot of η_{sp}/c versus c for polymethyl methacrylate (×), polymethylphenylsiloxane (+), polyvinylcarbazole (○) and polystyrene (●).

more than 10 per cent in the viscosity of a solution of polystyrene with the molecular weight 8,000,000, according to works by Lohmander and Svensson [13] and Lohmander [14].

The intrinsic viscosity, $[\eta]$, was obtained as the limiting value of the specific viscosity over the concentration, η_{sp}/c, as the concentration approaches zero. Details for four different polymer-solvent systems are shown in Fig. 5 by way of example. The results of the viscosity measurements are given in Table 1, in which each polymer is characterized principally by its intrinsic viscosity. As the constants a and K in the modified Staudinger equation

$$[\eta] = K \cdot M^a \tag{1}$$

are available in the literature for most of the polymer-solvent systems, the molecular weight, M, has also been computed and is given in Table 1. In the search for literature data on a and K, references given by Meyerhoff [15] and Stuart [16] have been of great help.

The molecular weight obtained in this way is the viscosity average molecular weight, M_v. As it can be expected that the investigated polymers are rather polydisperse, the difference between M_v and, in particular, the number average molecular weight, M_n, will be considerable. The average molecular weight used by the different investigators in the determination of a and K in equation (1) has therefore also been given in Table 1. Besides the already mentioned molecular weights, M_w denotes weight average molecular weight and M_{sD} indicates that a and K are based on molecular weight determinations from sedimentation and diffusion measurements. In some cases only the exponent a is given in the table, which is due to the fact that in the corresponding literature references, the data are not presented in a form which

Table 1. Results of the determination of the intrinsic viscosity of different polymer-solvent systems.

The symbols n, v, w and sD denote respectively M_n, M_v, M_w and M_{sD}.

Substance	Solvent	Temperature of the experiment, °C	$[\eta]$ ml/g	Molecular weight	$K \cdot 10^2$ ml/g	a	Reference and type of molecular weight average given by the author
Cellulose acetate co-butyrate	Acetone	25	189	97,000	1.37	0.83	17 *n*
Cellulose triacetate	Chloroform	25	230	250,000[a]		1.02	18 *v*
Dextran	Water	20	37.2	160,000	24.3	0.42	19 *w*
Ethyl cellulose	Methanol	25	142	190,000	5.23	0.65	20 *w*
Hydroxyethyl cellulose	Water	20	835[b]	470,000		0.87	21 *w*
Nitrocellulose	Ethyl acetate	30	986	350,000	0.250	1.01	22 *w*
Nylon	90 % Formic acid	25	117	16,000	11	0.72	23 *n*
Poly-*n*-butyl acrylate	Acetone	25	21.5	46,000	0.685	0.75	24 *w*
Poly-*n*-butyl methacrylate	Methyl ethyl ketone	23	96.6	820,000	0.156	0.81	25 *w*
Polydimethylsiloxane	Toluene	20	8.4	9,400	2.00	0.66	26 *n*
Polydimethylsiloxane	Toluene	20	11.9	16,000			
Polyethyl acrylate	Acetone	30	24.8	34,000	2.55	0.66	27 *n*
Polyethylene glycol	Water	20	3.7	240		0.72[c]	28
Polyethylene glycol	Water	20	402	470,000			
Polyethyl methacrylate	Methyl ethyl ketone	23	77.6	410,000	0.283	0.79	29 *w*
Polyisobutylene	Cyclohexane	30	49.4	52,000			
Polyisobutylene	Cyclohexane	30	527	1,600,000	2.76	0.69	30 *n*
Polyisobutylene	Cyclohexane	30	1820	9,600,000			
Polymethacrylic acid	Methanol	26	67.1	62,000	24.2	0.51	31 *n*
Polymethyl methacrylate	Methyl ethyl ketone	25	42.8	190,000	0.68	0.72	32 *w*
Polymethyl methacrylate	Methyl ethyl ketone	25	83.4	480,000			
Polymethylphenylsiloxane	Toluene	25	132				
Polystyrene	Toluene	25	75.1	190,000	1.7	0.69	33 *w*
Polyvinyl acetal	Toluene	25	52.0				
Polyvinyl acetate	Methyl ethyl ketone	25	33.6	48,000	4.20	0.62	34 *sD*
Polyvinyl alcohol	Water	25	54.1	21,000	14.0	0.60	35 *sD*
Polyvinyl butyral	95 % Ethanol	25	122				
Polyvinyl carbazole	Chlorobenzene	25	117				
Polyvinyl chloride	Cyclohexanone	30	132	940,000	0.0841	0.87	36 *w*
Polyvinyl chloride co-acetate	Cyclohexanone	30	77.2				
Polyvinyl chloride co-vinylidene chloride	Cyclohexanone	30	77.4				
Polyvinyl isobutyl ether	Methyl ethyl ketone	30	27.7				
Polyvinyl methyl ether	Methyl ethyl ketone	30	29.4	15,000	13.7	0.56[c]	37 *w*
Polyvinylpyrrolidone	Water	25	16.0	29,000	5.65	0.55	38 *w*
Sodium carboxymethyl cellulose	Cadoxen	25	710	700,000		0.73	39 *w*

[a] The molecular weight was computed via the degree of polymerization, using a constant 398 given in the reference.

[b] This value was obtained from an investigation by Brown [77] on the same sample of hydroxyethyl cellulose as used in the present investigation.

[c] The quoted a-value may be erroneous, due to a misprint in the paper referred to.

fits into equation (1). The difference between the units cm^3/g and ml/g has been neglected in the computation of the molecular weights and also in the compilation of the K-values in Table 1.

Chapter 3. Compression measurements

a. *Experimental procedure*

A straightforward method for determining the volume decrease of a liquid under pressure is to weigh the trapped mercury after isolation and drying. This method is used, for instance, by Newitt and Weale [40] and Stutchbury [41]. As will be shown later, however, this volume can also be obtained by weighing the piezometer, first when empty, then when filled with polymer solution before being subjected to pressure, and finally with the trapped mercury and remaining polymer solution after the experiment.

Polymer solutions of five or six different concentrations were prepared. In general the concentrations were 0, 0.5, 1.0, 1.5, 2.0 and 2.5 per cent[1] with of course certain variations depending on the solubility of the polymer and the viscosity of the solutions. When the solvent was water one more concentration was added to the concentration range. The weighed piezometers were filled with the solutions and, with the stoppers upwards, were placed in a separate water thermostat, which was adjusted to the same temperature as the pressure vessel. As the ground glass joints were very tight, the piezometers could be immersed in the thermostat, so that the water covered the joints. No grease was used in the ground joints. The liquid surface in the capillary was so small that the evaporation could not introduce any serious error into the determination of the concentration. The piezometers were allowed to reach temperature equilibrium during a period of 20 minutes. Sometimes air bubbles were formed on the inside of the piezometer; this could be avoided, however, if the stock solutions were made up from boiled water or if they were warmed up some ten degrees above the temperature of the experiment before the piezometers were filled. After a second weighing, followed by another period of 20 minutes in the thermostat, the piezometers were enclosed in the steel capsule and transferred to the pressure vessel.

The pressure was increased very slowly to give time for the heat of compression to dissipate. Thirty minutes were allowed for a pressure increase up to 4500 atm, while an even slower rate was employed for reaching higher pressures. The piezometers were then held at the maximum pressure for 45 minutes to allow for temperature equilibrium. An uncertainty in the temperature of one or two tenths of a degree was of no importance, as all the piezometers have the same temperature and the change of the partial specific volume with temperature is small. For the decrease of pressure from 4500 atm to 1 atm a period of 90 minutes was allowed. The time for pressure increase and decrease at other pressures was chosen in relation to the given figures. Even though the release of pressure was as slow as mentioned above, the temperature of the pressure-transmitting liquid in the pressure vessel after an experiment could be as much as 1° lower than before the experiment. As the error of the temperature is in this direction, its influence on the density of the polymer solutions can be nullified by warming the piezometers in the thermostat to the original temperature before they are weighed for the third time.

Before each weighing the piezometers were dipped into acetone and wiped dry. Cooling and contraction of the contents of the piezometer accompanied the evaporation of acetone, so that the meniscus in the capillary sank 10 millimeters or more depending on the nature of the liquid. A slight rise in the temperature was not then

[1] In the early part of the investigation a pressure vessel holding only four piezometers was available. Therefore some of the substances have been investigated at fewer concentrations.

sufficient to bring the meniscus to the top of the capillary, where the solution could evaporate. A special holder, easily attachable to and removable from the piezometer, was designed to hang the piezometer on the arm of the balance. With the described technique it was possible to weigh such volatile liquids as ethyl acetate reproducibly to one milligram.

For the weighings, a Mettler analytical balance, type B 5, was used. The accuracy of the balance was checked by means of very accurate weights. Wherever necessary, corrections for the buoyancy of the air were made.

During preliminary experiments with the piezometers it proved necessary to clean them thoroughly to obtain reproducible results. Before each experiment they were therefore boiled in concentrated nitric acid for 15 minutes. After repeated rinses with distilled water they were boiled in distilled water and were then allowed to dry. To remove remaining polymer solution from the capillary tubes efficiently they were rinsed with ethanol and then boiled in nitric acid. A small amount of ethanol was permitted to remain in the capillary to react with the nitric acid.

b. *Computation of the compression from experimental results*

As mentioned above, the volume of the trapped mercury can be obtained without direct drying and weighing of the mercury. From the weight of the contents of the piezometer before and after pressure has been applied, the following expression can be derived for the volume at 1 atm of the trapped mercury, V_{Hg},

$$V_{Hg} = \frac{M_2 - M_1}{\varrho_{Hg} - \varrho_l}, \tag{2}$$

in which M_1 and M_2 are the weights of the contents of the piezometer before and after pressure has been applied. ϱ_{Hg} and ϱ_l denote the densities of the mercury and the liquid at 1 atm. The density of the mercury at the temperature of the experiment was taken from Beattie *et al.* [10], whereas the density of the liquid was calculated from the weight of the liquid and the volume of the piezometer. The density measurements thus performed were of gratifying accuracy. The standard deviation of the density is estimated to be $\pm 4 \cdot 10^{-5}$ g/ml from a large number of measurements (see p. 546). A comparison with literature data shows good agreement. For instance, from a rectilinear extrapolation to 20.0°C of densities measured in a temperature range of a few degrees around 20°C, the following densities were obtained: 0.90052, 0.70230, 0.86676 and 0.86402 g/ml for ethyl acetate, *n*-octane, toluene and *m*-xylene respectively. These data are in good or excellent agreement with those given by Timmermans [42] or Forziati *et al.* [43], which are 0.90056, 0.70252, 0.86683 and 0.86412 g/ml respectively.

This method of determining the volume of the trapped mercury is certainly as accurate as the method of drying and weighing. On comparing the two methods in four experiments the determined mercury volumes agreed extremely well, on an average within 0.01 %. The latter method always gave lower values than the former, which may be attributed to the difficulty of accumulating all the mercury drops on the walls of the piezometer. The method used here is under all circumstances less time-consuming.

From V_{Hg} it is now possible to calculate the compression of the liquid, which is a more useful quantity than its volume decrease. The compression or the relative volume decrease is defined as follows

$$k = -\frac{V_p - V_1}{V_1} = -\frac{\Delta V}{V_1}, \tag{3}$$

where V_1 and V_p are the total volume of the liquid at 1 atm and at the pressure p atm. The compression of the liquid is computed from V_{Hg} by means of the equation

$$k = \frac{V_{Hg}(1 - k_{Hg}) + V_s(1 - k_g)}{V} + k_g, \tag{4}$$

in which k_{Hg} and k_g denote the compression of the mercury and the Pyrex glass at the same pressure, V_s and V are the volumes of the stem and the piezometer at 1 atm respectively. The equation can be derived in the way suggested by Adams [1].

The compression of mercury was computed with the aid of a digital computer from an equation

$$\log \frac{L^2 P}{L_0 - L} = 5.8837 - 0.0004877\ T + 4.95(L_0 - L) \tag{5}$$

given in a paper by Bett *et al.* [44], where T denotes the temperature, P the pressure (in bars) and L is the length of one face of a cube containing unit mass of mercury and L_0 is the value of L at 1 atm. The value of L_0 at different temperatures was obtained from the earlier mentioned work by Beattie *et al.* [10]. Keeping T and consequently L_0 constant, equation (5) was solved with respect to L at different pressures. The compression of mercury, k_{Hg}, is then obtained as $(L_0^3 - L^3)/L_0^3$.

The compression of water, which was needed for the determination of the pressure in the vessel (see below), was obtained from data (corrected for misprints, see reference [45]) in a paper by Bridgman [46]. The digital computer was again used, this time to interpolate, by means of a polynomial of the second degree, the compression of water at smaller intervals along both the vertical (pressure) and horizontal (temperature) axes than those given by Bridgman.

The compression of Pyrex glass at different temperatures and pressures was computed by means of a second degree polynomial from a paper by Bridgman [47]. With the reservation that mercury and water are in the liquid state, their compression data and also those of glass, computed at pressure intervals of 100 kg/cm² in the range 1–12,000 kg/cm² and at temperature intervals of half a degree in the temperature region 0.0°–50.0°C, were compiled into tables, covering 300 pages, of which one page is shown in Fig. 6. The compression at the desired pressure and temperature was then obtained from these tables by a rectilinear interpolation.

Four copies of these tables are available at this Institute, and also the tape from the digital computer on which the final compression data of water and mercury are punched.

c. *The pressure determination*

The maximum pressure during an experiment was obtained by an indirect method suggested by Adams [48] which presupposes knowledge of the compression of water at different pressures and temperatures. For this purpose one of the seven piezometers in the pressure vessel was always filled with water. From the volume of the mercury trapped in it the maximum pressure was calculated by means of equation (4) by a procedure of successive approximations. The accuracy of such a pressure

T= 22.5

P KG/CM2	K H2O	K HG	K PYREX
4100	0.11490	0.01505	0.01233
4200	0.11676	0.01539	0.01263
4300	0.11859	0.01573	0.01294
4400	0.12039	0.01607	0.01324
4500	0.12216	0.01641	0.01354
4600	0.12392	0.01674	0.01385
4700	0.12566	0.01708	0.01415
4800	0.12738	0.01741	0.01446
4900	0.12907	0.01774	0.01476
5000	0.13074	0.01808	0.01507
5100	0.13240	0.01841	0.01537
5200	0.13404	0.01874	0.01568
5300	0.13565	0.01906	0.01598
5400	0.13725	0.01939	0.01629
5500	0.13883	0.01972	0.01660
5600	0.14038	0.02004	0.01690
5700	0.14192	0.02037	0.01721
5800	0.14344	0.02069	0.01751
5900	0.14493	0.02101	0.01782
6000	0.14641	0.02134	0.01813
6100	0.14788	0.02166	0.01843
6200	0.14933	0.02197	0.01874
6300	0.15076	0.02229	0.01905
6400	0.15218	0.02261	0.01935
6500	0.15358	0.02293	0.01966
6600	0.15497	0.02324	0.01997
6700	0.15636	0.02355	0.02028
6800	0.15773	0.02387	0.02058
6900	0.15909	0.02418	0.02089
7000	0.16044	0.02449	0.02120
7100	0.16177	0.02480	0.02151
7200	0.16309	0.02511	0.02182
7300	0.16439	0.02542	0.02212
7400	0.16568	0.02573	0.02243
7500	0.16696	0.02603	0.02274
7600	0.16823	0.02634	0.02305
7700	0.16950	0.02664	0.02336
7800	0.17075	0.02694	0.02367
7900	0.17199	0.02725	0.02398
8000	0.17322	0.02755	0.02429

Fig. 6. The compression of water, mercury and Pyrex glass at 22.5°C in the pressure region 4100–8000 kg/cm².

Table 2. Pressure determinations in four different experiments I, II, III, IV with piezometers containing water.

Expt. I		Expt. II		Expt. III		Expt. IV	
Piezometer No.	Pressure atm	Piezometer No.	Pressure atm	Piezometer No.	Pressure atm	Piezometer No.	Pressure atm
5	2722	9	4233	5	4778	13	8235
7	2745	10	4232	6	4777	24	8254
9	2742	11	4232	7	4763	25	8257
11	2742	12	4237	8	4784	26	8244
13	2736					27	8247
15	2734					28	8233
17	2742					29	8253
Average pressure	2738		4234		4776		8246
Maximum deviation from average pressure	0.59 %		0.07 %		0.27 %		0.16 %

measurement naturally depends on the reliability with which the quantities of equation (4) are determined. Among the compression data the compression of water is especially important, as it is roughly ten times larger than the other two. In the paper [46] Bridgman estimates that his own values may be in error by as much as 1 per cent at the higher pressures. Bridgman's values are constantly lower than those of Adams [1] and the agreement is better at the higher pressures. A direct comparison of Adams's values for the compression of water, expressed by a formula suggested by Gibson [8, 49], and Bridgman's values at the pressures at which the experiments of this investigation have been carried out, shows that the former values are between 0.5 and 1.6 per cent higher than the latter, with an average of 1.0 per cent. At present, however, Bridgman's compression data for water seem to be the only ones available up to 12,000 kg/cm^2 covering a temperature region of one hundred degrees.

Very large systematic errors in the pressure determination would on the other hand be disclosed by a comparison between the compression values of the pure solvents from the present investigation and those from literature data, since in the latter case another method of measuring the pressure was used. The result of such a comparison, shown in Table 6, gives no evidence of similar errors. It will also be shown later that, in general, the partial specific volume of a solute is less sensitive to variations in the pressure than is the specific volume of liquids. The method of pressure determination used here can therefore be regarded as sufficiently accurate for its purpose.

The reproducibility of the pressure determinations with piezometers was tested by simultaneously subjecting to pressure several piezometers all containing water. The results of four such experiments are shown in Table 2. The large deviation of one or two values from the others in each experiment can be mainly ascribed to the uncertainty as to whether or not the last drop of mercury flows into the piezometer. Gibson [7] has determined the volume of mercury drops from a glass piezometer in a pressure vessel equipped with windows. He found that the volume of the drops varied considerably. In the case of water the variation was between 0.002 0.003 ml, whereas

the volume was 0.0015 ml when the piezometer contained a 10 % solution of lithium bromide. From a comparison of Gibson's results and Adams's [1] estimation of the volume of the mercury drops, it is apparent that the real volume is much larger than that which is obtained by a computation from the diameter of the orifice of the capillary tube. It is obvious that the uncertainty about the last drop of mercury may under unfavourable circumstances introduce an error into the pressure measurements amounting to several tenths of a per cent. Provided the size of the drops is the same throughout the pressure region the relative pressure determination will be more uncertain at the lower pressures. As an average for the whole pressure region investigated the relative error in the pressure determination is estimated to be 0.3 per cent, whereas the magnitude of the absolute error will be somewhat uncertain until the accuracy of Bridgman's compression data is known. To avoid a systematic error in the pressure determination caused by a possible defect in a piezometer, the piezometer containing water was changed from experiment to experiment.

This method of determining the pressure by means of a piezometer containing water also provided, with every experiment, an extra check on the volume of the piezometer used. No change of that volume after long-term use could be observed.

d. *The Tait equation*

Gibson *et al.* [49–54] have determined the compression of many liquids and salt solutions under pressures up to 1000 bars. They have found that the isothermal compression of the investigated liquids or solutions, within the limits of experimental error, can be expressed with the aid of the equation

$$k = C \log \frac{B+p}{B+1}, \tag{6}$$

where p denotes the pressure and B and C are constants. The equation was originally proposed in the differential form by Tait [55], who used it to express the compressibility of water as a function of pressure. It has later been applied by Carl [56] to the compression data of Amagat and Bridgman on some liquids, mostly organic. The theoretical significance of the constant B has been discussed by Gibson and Kincaid [50] and Gibson and Loeffler [51], who concluded that B represents the difference between the cohesive pressure due to temperature independent attraction between the molecules and the expansive pressure due to thermal energy of the molecules. This assumption is consistent with the fact that B varies with temperature. The constant C, on the other hand, has proved to be almost temperature independent and also shows very little variation with the composition of the liquid.

Since the right hand side of equation (6) approaches infinity at extremely high pressures, whereas the left hand side cannot exceed unity, it is obvious that the equation cannot be applied over very extensive pressure regions. In a modified form, however, the equation has been used to represent the compression of water up to 25,000 atm [57].

Although the Tait equation has a remarkable ability to fit compression data for many liquids as well as some solids, there has not until quite recently been any interpretation of the theoretical significance of B and C based on a theory for liquids. In a series of papers Ginell [58–60] has derived the Tait equation from the association theory and discussed the meaning of the above-mentioned constants. According to

Ginell B is not a true constant, although its variation with pressure is small in the pressure range up to 1000 atm. Assuming that liquids consist of clusters of molecules and holes, B is in the main a measure of the excluded volume of these clusters and C is a measure of the change in the volume of the holes; moreover according to the same author, C is not a constant but rather a slowly varying factor. Indications in this direction can also be found in the paper by Carl [56].

Each experiment gave at the maximum pressure the compression of the pure solvent and the series of solutions of five or six different concentrations. The compressions were calculated by means of equation (4) from the volume of the trapped mercury. Some of the solvents, e.g. toluene, tetrachloroethane and methyl isobutyl ketone, were used as solvents for several different polymers. For these solvents a large amount of compression data at different pressures was obtained and the Tait equation was fitted to these data by the method of least squares.

The main features of the calculations are as follows. The function

$$z = \sum_i \left(C \log \frac{B + p_i}{B + 1} - k_i \right)^2 \tag{7}$$

is formed in which B and C are to be determined so as to give a minimum value of z. After taking the partial derivatives of z with respect to B and C and setting $\partial z/\partial B = 0$ and $\partial z/\partial C = 0$ in the usual manner, the following equations are obtained

$$C = \frac{\sum_i k_i \log \dfrac{B + p_i}{B + 1}}{\sum_i \left(\log \dfrac{B + p_i}{B + 1} \right)^2}, \qquad C = \frac{\sum_i k_i \dfrac{p_i - 1}{(B + 1)(B + p_i)}}{\sum_i \dfrac{p_i - 1}{(B + 1)(B + p_i)} \log \dfrac{B + p_i}{B + 1}}. \tag{8 a, b}$$

In solving the system of equations C is eliminated and the equation

$$\sum_i k_i \log \frac{B + p_i}{B + 1} \sum_i \frac{p_i - 1}{(B + 1)(B + p_i)} \log \frac{B + p_i}{B + 1} - \sum_i k_i \frac{p_i - 1}{(B + 1)(B + p_i)} \sum_i \left(\log \frac{B + p_i}{B + 1} \right)^2 = 0 \tag{9}$$

solved by successive approximations. A somewhat simpler equation than (9) can be derived from equation (7) if 1 is considered to be negligible by comparison with B. As the computations proved to be tedious, this simpler equation was first solved by successive approximations and then the obtained B-value needed only to be slightly corrected to satisfy equation (9). To check the calculations the C-value was finally computed by means of both equations (8a) and (8b).

Chapter 4. Results of compression measurements

a. *Compression and compressibility of solvents. Comparison with literature data*

The results of the compression measurements for toluene, *sym*-tetrachloroethane and methyl isobutyl ketone are shown in Table 3. Although the compression measurements for each substance have been performed at different temperatures, it can be

Table 3. Experimentally obtained compression data (k_{exp}) for toluene at 22.3°C, *sym*-tetrachloroethane at 22.1°C and methyl isobutyl ketone at 22.4°C compared with data calculated by the Tait equation (k_{calc}).

Toluene				*sym*-Tetrachloroethane				Methyl isobutyl ketone			
p atm	k_{exp}	k_{calc}	Dev. %	p atm	k_{exp}	k_{calc}	Dev. %	p atm	k_{exp}	k_{calc}	Dev. %
676	0.04578	0.04513	+1.42	1404	0.06151	0.06149	+0.03	2420	0.12228	0.12274	−0.38
759	0.05092	0.04952	+2.75	2620	0.09501	0.09501	0.00	2431	0.12242	0.12306	−0.52
1500	0.08272	0.08202	+0.85	2674	0.09628	0.09626	+0.02	2448	0.12296	0.12355	−0.48
1513	0.08305	0.08250	+0.66	2686	0.09646	0.09654	−0.08	2449	0.12305	0.12358	−0.43
1540	0.08430	0.08351	+0.94	4271	0.12783	0.12771	+0.09	2617	0.12871	0.12831	+0.31
2359	0.10971	0.11002	−0.28	4422	0.13010	0.13023	−0.10	2623	0.12927	0.12847	+0.62
2567	0.11550	0.11578	−0.24	4490	0.13131	0.13134	−0.02	2633	0.12992	0.12875	+0.90
2627	0.11609	0.11738	−1.11	4532	0.13207	0.13203	+0.03	4482	0.16851	0.16959	−0.64
3053	0.12767	0.12808	−0.32					4526	0.17096	0.17038	+0.34
4357	0.15488	0.15521	−0.21					4531	0.17169	0.17047	+0.71
4388	0.15512	0.15577	−0.42					4699	0.17307	0.17344	−0.21
4391	0.15512	0.15583	−0.46					4768	0.17412	0.17463	−0.29
4539	0.15697	0.15848	−0.96					4785	0.17492	0.17493	−0.01
5677	0.17700	0.17683	+0.10								
6896	0.19409	0.19339	+0.36								
7756	0.20528	0.20363	+0.80								
Average of dev. %			0.74				0.05				0.45

regarded as legitimate to compile them, since the alteration of the compression for a small temperature change is certainly masked by the experimental errors. All the compression data in Table 3 were used for the computation of B and C of the Tait equation. To give an idea of how close the logarithmic function fits the experimental data, k_{exp}, the calculated compression values, k_{calc}, together with the per cent deviations, $100(k_{exp}-k_{calc})/k_{exp}$, are given as well as an average of the per cent deviations without regard to the sign of the deviation. The agreement between experimental and computed compression values is quite different for the three liquids; this is probably a result of the different nature of the three liquids. In this connection it

Table 4. B and C of the Tait equation for cyclohexanone, formic acid (98–100 %), methyl ethyl ketone, methyl isobutyl ketone, *sym*-tetrachloroethane and toluene.

Liquid	Temperature °C	Pressure range atm	B atm	C
Cyclohexanone	23.3	1566–2626	1345	0.20683
Formic acid (98–100 %)	22.4	755–1061	1493	0.21186
Methyl ethyl ketone	10.0	1687–3011	955	0.22045
	20.0	1700–2965	881	
	35.0	1657–2932	774	
Methyl isobutyl ketone	22.4	2420–4785	982	0.22765
sym-Tetrachloroethane	22.1	1404–4532	1653	0.23049
Toluene	22.3	676–7756	1205	0.23379

Table 5. Comparison of the compressibilities at 1 atm of methanol, ethanol, ethyl ether, acetone, toluene, carbon disulphide and water taken from different sources.

The compressibilities are expressed in atm^{-1}. Temperature 20°C.

Liquid	Gibson 1000 bars	Amagat 3000 atm	This investigation 7756 atm	Bridgman 12000 kg/cm²	Freyer *et al.*	Tyrer
Methanol	$122.9 \cdot 10^{-6}$	$107.9 \cdot 10^{-6}$		$96.7 \cdot 10^{-6}$	$123.4 \cdot 10^{-6}$	$122.7 \cdot 10^{-6}$
Ethanol		106.0		102.1	111.3	113.1
Ethyl ether		176.7		133.6	186.8	189.0
Acetone		115.5		109.5	129.2	
Toluene			$82.9 \cdot 10^{-6}$		90.6	90.8
Carbon disulphide		89.0		92.2	93.1	93.8
Water	46.9			47.8		46.5

can be noted that Carl [56] also found fair agreement for some liquids and good agreement between experimental and computed values for others in his investigation of the compression data of Amagat and Bridgman. The constants B and C of the Tait equation for toluene, tetrachloroethane and methyl isobutyl ketone are given in Table 4. As there do not seem to be any compression data published for cyclohexanone, formic acid and methyl ethyl ketone, the constants B and C have also been given for these liquids, but it should be noted that they have been determined on a basis of only two or three compression measurements for each liquid and temperature.

The compressibility, β, is defined as

$$\beta = -\frac{1}{V_1}\left(\frac{\partial V}{\partial p}\right)_T, \tag{10}$$

where V_1 is the volume of the liquid at 1 atm, p denotes the pressure and T the temperature. With the definition of the compression, k, in mind, equation (10) can also be written as $\beta = dk/dp$, from which it is apparent that at high pressures the compressibility (isothermal) for a liquid is easily obtainable from the Tait equation. If, however, the compressibility of toluene is calculated by means of the Tait equation at 1 atm, which is far outside the pressure range investigated, it fails to given an accurate value. This shortcoming is clearly demonstrated in Table 5, where the computed compressibility of toluene at 1 atm is compared with those from literature data given by Tyrer [61] and Freyer *et al.* [62], who have obtained them from experiments performed at or near 1 atm. In order to throw further light upon the problem, the compressibilities of some other liquids [7, 63, 56] computed from the Tait equation are also given in Table 5. A comparison between the compressibilities given by the different sources reveals that in almost all cases the compressibilities for each liquid calculated by means of the extrapolated Tait equation are too low. The table also shows that the agreement between the compressibilities measured directly at 1 atm and those computed from the Tait equation usually improves as the maximum pressure of the pressure range investigated becomes smaller; this is especially noticeable from the results of Gibson. This is not wholly unexpected, as it is in general easier to derive a function of approximate validity in a small interval than in a large one, but it points to the fact that the constant B is not pressure independent over large pressure ranges.

Table 6. A compilation of compression data at 25°C from different sources for some liquids used as solvents in the present investigation.

The numbers of the references are given below the names of the authors.

Liquid	Pressure atm	This investigation	Newitt *et al.* [40]	Eduljee *et al.* [95]	Bridgman [97, 64]	Gibson extrapol. [52]
n-Amyl alcohol[a]	2626	0.1130			0.1197	
	4514	0.1524			0.1589	
Chlorobenzene	2588	0.1056			0.1065	0.1060
	4462	0.1446			0.1453	0.1434
Ethyl acetate	4600	0.1788			0.1797	
n-Octane	2620	0.1401		0.1391	0.1384	
	4530	0.1836		0.1812	0.1814	
sym-Tetrachloroethane	400	0.0221	0.0220			
	500	0.0268	0.0268			
	600	0.0314	0.0315			
	700	0.0359	0.0360			
	900	0.0442	0.0441			
	1000	0.0480	0.0478			
m-Xylene	1727	0.0880			0.0899	
	2998	0.1224			0.1260	

[a] The compression data for *n*-amyl alcohol are given at 20°C.

A comparison between the compression values for the solvents used in this study obtained by the author and those given in the literature is of value as a test of the reliability of the pressure scale employed, which is based on Bridgman's compression data for water. Compression values from the literature have therefore been compiled in Table 6. The compression data of this investigation have been converted to 25°C except in the case of *n*-amyl alcohol, for which the compression data of Bridgman are given at 20°C.

An inspection of Table 6 reveals that there is no reason to believe that the pressure scale is affected by any large systematic error, since the compression results of this investigation agree fairly well with literature data. The only case with a conspicuously high discrepancy between compression values is amyl alcohol, and the deviation is here difficult to explain. It can be noted, however, that Bridgman [64] has on one occasion reported still larger discrepancies among his own compression values from different times. Other high pressure data which can be mentioned in this connection are the compressibilities of toluene, $80.6 \cdot 10^{-6}$ atm^{-1}, at 114.5 atm and 25°C reported by Ritzel [65] and of cyclohexanone, $58.5 \cdot 10^{-6}$ atm^{-1}, at 20°C in the pressure range 100–300 bars by Richards [66], which also show good agreement with the present results, $79.9 \cdot 10^{-6}$ atm^{-1} and $58.6 \cdot 10^{-6}$ atm^{-1} respectively, computed by means of equation (6) with constants taken from Table 4 and converted to the respective temperatures given above.

b. *Compression of solutions and concentration dependence of the compression*

Factors determining the compressibility and compression of aqueous solutions of low molecular weight substances have been discussed by Richards and Chadwell

Table 7. The compression, k, of water solutions of glucose and polyvinylpyrrolidone at 4500 atm.

The concentration, x_2, of the solute is given as a weight fraction.

Glucose		Polyvinylpyrrolidone	
x_2	k	x_2	k
0	0.12487	0	0.12487
0.010192	0.12413	0.004784	0.12490
0.020444	0.12322	0.009260	0.12459
0.030578	0.12248	0.013910	0.12429
0.040722	0.12171	0.018453	0.12383
0.050980	0.12087	0.023203	0.12345
0.060095	0.11979	0.028249	0.12332

[67] and by Gibson [8, 68]. The former authors have investigated water solutions of ether, methyl acetate and urethan and have found that these substances, at the same concentration, decrease the compressibility of water to the same extent provided the solutions are diluted. This decrease, which was discovered at an early date by Drucker [69], is especially pronounced among electrolytes, since the ions function like the molecules of undissociated substances. Gibson has shown that among the electrolytes many solutions of unhydrolyzed sulphates at the same concentration have the same compression. Among other electrolytes he has also observed great regularity in their influence on the compression of water. The anomalous behaviour of certain salts, such as lithium chloride, has been ascribed to the fact that not all ions have the same ability to depolymerize water.

The compression at constant pressure of the solutions investigated was in almost all cases decreased by increasing concentration. As typical of the whole investigation, the compressions at different concentrations of glucose, polyvinylpyrrolidone, sodium polymethacrylate and sodium carboxymethyl cellulose are given in Tables 7 and 8. For the purpose of comparison, the compressions are given at the same pressure, 4500 atm. The solutions of sodium polymethacrylate and sodium carboxymethyl cellulose in 0.01 M NaOH can in this respect be regarded as water solutions

Table 8. The compression, k, of solutions of sodium polymethacrylate and sodium carboxymethyl cellulose in 0.01 M NaOH at 4500 atm.

The concentration, x_2, of the solute is given as a weight fraction.

Sodium polymethacrylate		Sodium carboxymethyl cellulose	
x_2	k	x_2	k
0	0.12487	0	0.12487
0.007223	0.12376	0.001004	0.12479
0.014429	0.12241	0.002018	0.12468
0.021387	0.12134	0.003023	0.12463
0.028472	0.11991	0.003986	0.12457

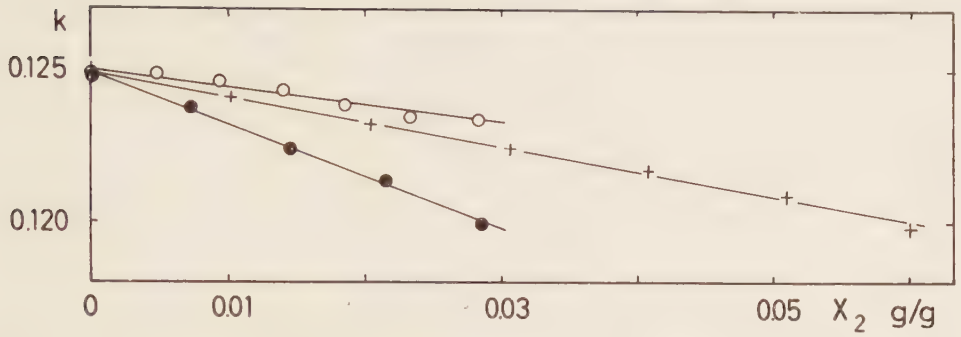

Fig. 7. The compression at 4500 atm of solutions of polyvinylpyrrolidone (○), glucose (+) and sodium polymethacrylate (●) as a function of the concentration of the solute expressed as a weight fraction.

since the concentration of sodium hydroxide is so small that it has a negligible effect on the compression of water. Glucose was included in the investigation for a comparison between the influence of a low molecular weight substance and a polymer on the compression of water.

When the compression was plotted against the concentration, x_2, expressed as a weight fraction, a rectilinear relationship between them was obtained within experimental error in the concentration ranges investigated. This is illustrated in Fig. 7 for three of the substances in Tables 7 and 8. The slope of the lines, which is the change of the compression with concentration at constant pressure, $(\partial k/\partial x_2)_p$, was computed according to the method of least squares with the aid of the digital computer. (The letter p, denoting that the partial derivative is taken at constant pressure, will be omitted in the text unless ambiguity might arise.) The standard deviation of $\partial k/\partial x_2$ and k was obtained simultaneously.

Throughout the entire investigation the compression changed very little from that of the pure solvent to that of the solution with the highest concentration, due to the narrow concentration ranges which were investigated. This is exemplified in Tables 7 and 8. B of the Tait equation will therefore undergo only small variations when computed for the pure solvent and the different solutions, as is illustrated in Table 9.

The compression-concentration relations for solutions of polystyrene in toluene were studied at eight different pressures in the concentration range 0–2.5 %. The $\partial k/\partial x_2$-values are given in Table 10. Though these values are somewhat irregular, due

Table 9. The constant B of the Tait equation at different concentrations of ethyl cellulose in *sym*-tetrachloroethane and of polyethyl methacrylate in methyl isobutyl ketone.

B is given in atm.

Concentration %	0	0.5	1.0	1.5	2.0	2.5
Ethyl cellulose in *sym*-tetrachloroethane	1653	1658	1663	1668	1674	1680
Polyethyl methacrylate in methyl isobutyl ketone	982	982	985	989	992	995

Table 10. The concentration dependence of the compression, $\partial k / \partial x_2$, of toluene solutions of polystyrene at different pressures.

Temperature 22.7°C.

Pressure atm	$-\frac{\partial k}{\partial x_2} \cdot 10^2$
759	3.0
1540	3.8
2359	3.8
3053	4.2
4357	4.9
5677	5.2
6896	5.8
7756	6.5

to experimental errors, it is quite clear that $-\partial k / \partial x_2$ increases with increasing pressure. In other words the dissolved substance has a greater influence on the compression at high pressures than at low at a given concentration.

For other polymer solutions similar investigations were carried out at one or two different pressures. To facilitate a comparison the $\partial k / \partial x_2$-values were converted to the pressures 2500 atm and 4500 atm. The result for a series of water solutions is found in Tables 11 and 12. From an inspection of Table 11 it is apparent that the increase of $-\partial k / \partial x_2$ with pressure which was observed in polystyrene solutions is also found in water solutions of other polymers. A comparison between glucose and the polymers in Table 11 reveals that the effect of the dissolved substance, whether low molecular or macromolecular, on the compression of water is rather similar. Accepting for $\partial k / \partial x_2$ an error of $\pm 0.5 \cdot 10^{-2}$, which is the average of a large number of computed standard deviations of $\partial k / \partial x_2$, the effects on the compression of water of many of the substances in Table 11 are hardly distinguishable from one another. The same small difference between the $\partial k / \partial x_2$-values is also noticed among the acrylates

Table 11. Values of $\partial k / \partial x_2$ at 2500 and 4500 atm for different substances dissolved in water.

Temperature 21.5°C.

Substance	Concentration range %	$-\left(\frac{\partial k}{\partial x_2}\right) \cdot 10^2$ $p = 2500$	$-\left(\frac{\partial k}{\partial x_2}\right) \cdot 10^2$ $p = 4500$
Glucose	0–6.0		8.0
Dextran	0–3.8	5.3	7.0
Hydroxyethyl cellulose	0–1.0		5.5
Polyvinyl alcohol	0–2.8	5.1	7.4
Polyvinylpyrrolidone	0–2.8	4.6	6.4
Polyethylene glycol			
($M_v = 240$)	0–3.0	5.0	6.3
($M_v = 470{,}000$)	0–2.4	5.0	6.1
Serum albumin (bovine)	0–3.8	3.3	

Table 12. Values of $\partial k/\partial x_2$ for different solutions of polyelectrolytes and electrolytes at 4500 atm.

Temperature 21.1°C for polyelectrolytes, 25.0°C for electrolytes.

Substance	Solvent	Concentration range %	$-\left(\frac{\partial k}{\partial x_2}\right)\cdot 10^2$ $p = 4500$
Sodium polymethacrylate	0.01 *M* NaOH pH 12.0	0– 2.8	17.0
Sodium carboxymethyl cellulose	0.01 *M* NaOH pH 12.0	0– 0.4	8.4
Polymethacrylic acid	0.01 *M* HCl pH 2.0	0– 5.6	5.9
Sodium chloride	Water	0–25.0	14.8
Ammonium nitrate	Water	0–45.0	7.1
Potassium sulphate	Water	0–10.0	14.1

Table 13. Values of $\partial k/\partial x_2$ at 2500 and 4500 atm for different polymers dissolved in methyl isobutyl ketone.

Temperature 22.5°C.

Substance	Concentration range %	$-\left(\frac{\partial k}{\partial x_2}\right)\cdot 10^2$ $p = 2500$	$-\left(\frac{\partial k}{\partial x_2}\right)\cdot 10^2$ $p = 4500$
Polymethyl methacrylate	0–2.0	5.1	4.8
Polyethyl methacrylate	0–2.5	4.7	5.2
Poly-*n*-butyl methacrylate	0–2.8	4.6	5.1
Polyethyl acrylate	0–2.5	3.7	4.0
Poly-*n*-butyl acrylate	0–2.6	4.3	4.8

Table 14. Values of $\partial k/\partial x_2$ at 2500 and 4500 atm for different polymers dissolved in toluene.

Temperature 21.8°C.

Substance	Concentration range %	$-\left(\frac{\partial k}{\partial x_2}\right)\cdot 10^2$ $p = 2500$	$-\left(\frac{\partial k}{\partial x_2}\right)\cdot 10^2$ $p = 4500$
Polystyrene	0–2.5	3.9	5.0
Polyvinyl acetal	0–2.5	3.9	5.1
Polydimethylsiloxane	0–2.5	−0.6	−1.0
Polymethylphenylsiloxane	0–2.5		−0.5

and methacrylates in Table 13. Here $\partial k/\partial x_2$ is also relatively independent of the pressure. Returning to Table 11 and comparing the $\partial k/\partial x_2$-values at 4500 atm with corresponding values in Table 12, it is obvious that the polyelectrolytes decrease the compression of the solvent considerably more than the nonpolyelectrolytes. As pointed out before, sodium hydroxide has a negligible effect on the compression of water, due

Table 15. Values of $\partial k/\partial x_2$ at 2500 and 4500 atm for different polymer solutions. Temperature 21.8°C.

Substance	Solvent	Concentration range %	$-\left(\frac{\partial k}{\partial x_2}\right)\cdot 10^2$ $p = 2500$	$-\left(\frac{\partial k}{\partial x_2}\right)\cdot 10^2$ $p = 4500$
Nitrocellulose	Ethyl acetate	0–0.8		7.5
Ethyl cellulose	*sym*-Tetrachlororethane	0–2.5	3.9	4.0
Cellulose triacetate	*sym*-Tetrachlororethane	0–2.0	4.3	5.8
Cellulose acetate co-butyrate	*sym*-Tetrachlororethane	0–2.5	4.6	5.5
Polyvinyl chloride	Cyclohexanone	0–2.5	3.1	
Polyvinyl acetate	Cyclohexanone	0–2.5	1.7	
Polyvinyl chloride co-acetate	Cyclohexanone	0–2.6	2.5	
Polyvinyl methyl ether	*n*-Amyl alcohol	0–2.4	2.4	2.9
Polyvinyl isobutyl ether	*n*-Amyl alcohol	0–2.5	0.2	0.8
Polyvinyl butyral	*n*-Amyl alcohol	0–2.4	3.9	5.1
Polyvinylcarbazole	Chlorobenzene	0–2.5	5.5	6.7
Polyisobutylene				
($M_v = 52{,}000$)	*n*-Octane	0–2.5	6.0	6.9
($M_v = 1{,}600{,}000$)	*n*-Octane	0–2.6	6.4	7.6
($M_v = 9{,}600{,}000$)	*n*-Octane	0–1.2	5.6	8.0
Polydimethylsiloxane	Methyl ethyl ketone	0–2.5	−1.0	
Polymethyl methacrylate	*m*-Xylene	0–1.2	3.3	

to its low concentration. Also included in Table 12 are the $\partial k/\partial x_2$-values at 25°C for sodium chloride, potassium sulphate and ammonium nitrate, which have been computed from compression data of Adams and Gibson [1, 70, 71]. These electrolytes have an effect on the compression of water which is of the same order of magnitude as that given by the polyelectrolytes.

The polymers given in Tables 14 and 15 show a greater variation of the compression-concentration dependence. The numerically low values of $\partial k/\partial x_2$ for polyvinyl isobutyl ether are especially noticeable and even more so the values for the polysiloxanes which indicate that the solutions of these polymers are more compressible than the solvents themselves. The anomalous behaviour of the polysiloxanes reappears, as will be seen below, in the determination of the partial specific volume at high pressures. In fact the fractional decrease with pressure of the partial specific volume of the two polysiloxanes is larger than the compression of the solvent at the same pressure.

To determine whether the molecular weight of the dissolved polymer has any influence on the compression of the solution, three fractions of polyisobutylene in *n*-octane and two fractions of polyethylene glycol in water were investigated. As can be seen from the results in Tables 11 and 15, the effect of the molecular weight dependence of $\partial k/\partial x_2$ is so small that it is masked by the experimental errors ($\pm 0.5\cdot 10^{-2}$), if it exists at all.

c. *Discussion of the error of the compression measurements*

The method of measuring simultaneously the compression of several solutions with different concentrations, generally gives such a high accuracy for the difference between the compression of the solutions that k has to be expressed to five decimal places; if this is not done, rounding-off errors might be introduced in the determination of these differences. It must be remembered, however, that k itself is not determined to a higher accuracy than that expressed by four decimal places.

The magnitude of the standard deviation of k varied considerably from experiment to experiment, but as a rule only influenced the fifth decimal place. The standard deviation was computed for more than one hundred compression-concentration determinations performed in the whole pressure range from 676–7756 atm. As an average of all these standard deviations for k the value $\pm 6 \cdot 10^{-5}$ was obtained.

With the aid of this value the error of the pressure determination by the indirect method described earlier can be estimated. By differentiating the Tait equation for water [8], $k = 0.3071 \log (2923 + p) - 2923$, a relationship between dk and dp is obtained, which at the lower and upper limit of the investigated pressure range gives an error for the pressure determination of 1.6 atm and 4.9 atm respectively. These results are consistent with, though a little more favourable than, those which were obtained in the experiments described in Section 3 *c*. They also confirm that the pressure determination is relatively more uncertain at low pressures.

Chapter 5. The partial specific volume

a. *Definition of the partial specific volume. The relation between the partial specific volume and the apparent specific volume*

The partial specific volume of the solute, $\bar{v}_2$, in a binary solution is defined as

$$\bar{v}_2 = \left(\frac{\partial V}{\partial m_2}\right)_{m_1 T p}, \tag{11}$$

where V is the volume of the solution containing m_2 grams of the solute dissolved in m_1 grams of the solvent. As indicated, the partial derivative is to be taken at constant mass m_1, temperature T, and pressure p. The partial specific volume of the solvent, $\bar{v}_1$, is defined by interchanging the positions of subscripts 1 and 2 in the partial derivative. If m_2 and m_1 are instead expressed in moles, $\bar{v}_1$ and $\bar{v}_2$ will denote partial molal volumes. Expressed in words, equation (11) means that $\bar{v}_2$ is the volume increase of an infinitely large amount of solution when 1 g of the solute is added.

The concept of partial quantities was introduced in 1907 by G. N. Lewis [72]. In the original paper Lewis points out that an important difference between the partial molal volume of a dissolved substance and its molal volume in the pure state is that the latter is always positive whereas the former does not need to be so. A simple physical interpretation of the partial volume is therefore difficult. However, its usefulness in thermodynamic reasoning is undisputed.

Using the same notations as in (11) the volume of a binary solution can be written as

$$V = m_1 \bar{v}_1 + m_2 \bar{v}_2. \tag{12}$$

The apparent specific volume, φ_2, is defined by a similar equation

$$V = m_1 v^0 + m_2 \varphi_2, \tag{13}$$

where v^0 denotes the specific volume of the pure solvent. Taking the total differential of (12) and (13) and bearing in mind that $m_1\,d\bar{v}_1+m_2\,d\bar{v}_2=0$, the following equations are obtained

$$dV=\bar{v}_1dm_1+\bar{v}_2dm_2, \tag{14}$$

$$dV=v^0dm_1+m_2d\varphi_2+\varphi_2dm_2 \tag{15}$$

which give

$$d\varphi_2=\frac{\bar{v}_1-v^0}{m_2}dm_1+\frac{\bar{v}_2-\varphi_2}{m_2}dm_2 \tag{16}$$

and

$$\bar{v}_2=\varphi_2+m_2\frac{\partial\varphi_2}{\partial m_2}. \tag{17}$$

Writing the right hand side of (17) as $\partial(m_2\varphi_2)/\partial m_2$ and integrating results in the following equation

$$\varphi_2=\frac{1}{m_2'}\left(\text{constant}+\int_0^{m_2'}\bar{v}_2dm_2\right). \tag{18}$$

The constant is zero since $\varphi_2=\bar{v}_2$ when $m_2'\to 0$. Equation (19)

$$\varphi_2=\frac{1}{m_2'}\int_0^{m_2'}\bar{v}_2dm_2 \tag{19}$$

then gives one more relationship between φ_2 and $\bar{v}_2$.

From equation (19) it follows that $\varphi_2=\bar{v}_2$ in the concentration ranges where $\bar{v}_2$ is independent of the concentration. This proved to be the case for all substances in the relatively low concentration ranges studied in the present investigation. From the relation $m_1\,d\bar{v}_1+m_2\,d\bar{v}_2=0$ it then also follows that the partial specific volume of the solvent is independent of its concentration.

b. *Computation of the partial specific volume from experimental results*

Different ways, both analytical and graphical, of determining the partial specific volume from experimental data have been described by Lewis and Randall [73], Kraemer [74] and in a recent paper by Franks and Johnson [75]. In the present investigation the method which directly follows the definition (11) has been applied, which means that the volume of a solution containing a constant amount of solvent has been determined for different m_2-values. The volume, v_1, of a solution containing x g of the solute dissolved in 1 g of the solvent has been plotted versus x. A rectilinear relationship, $v_1=(\bar{v}_2)_1x+l$ (the subscript 1 in v_1 and $(\bar{v}_2)_1$ refers to the pressure 1 atm), within the accuracy of the data has thereby been obtained for the substances investigated (Fig. 8). The slope of the line, $(\bar{v}_2)_1$, is the partial specific volume of the solute. The straight line representing the above equation was located by means of the method of least squares with the aid of the digital computer.

A division of equation (12) by the total weight of the solution, m_1+m_2, followed by a replacement of $m_2/(m_1+m_2)$ by the concentration x_2 and of $\bar{v}_1$ by v^0, gives after a few rearrangements the equation

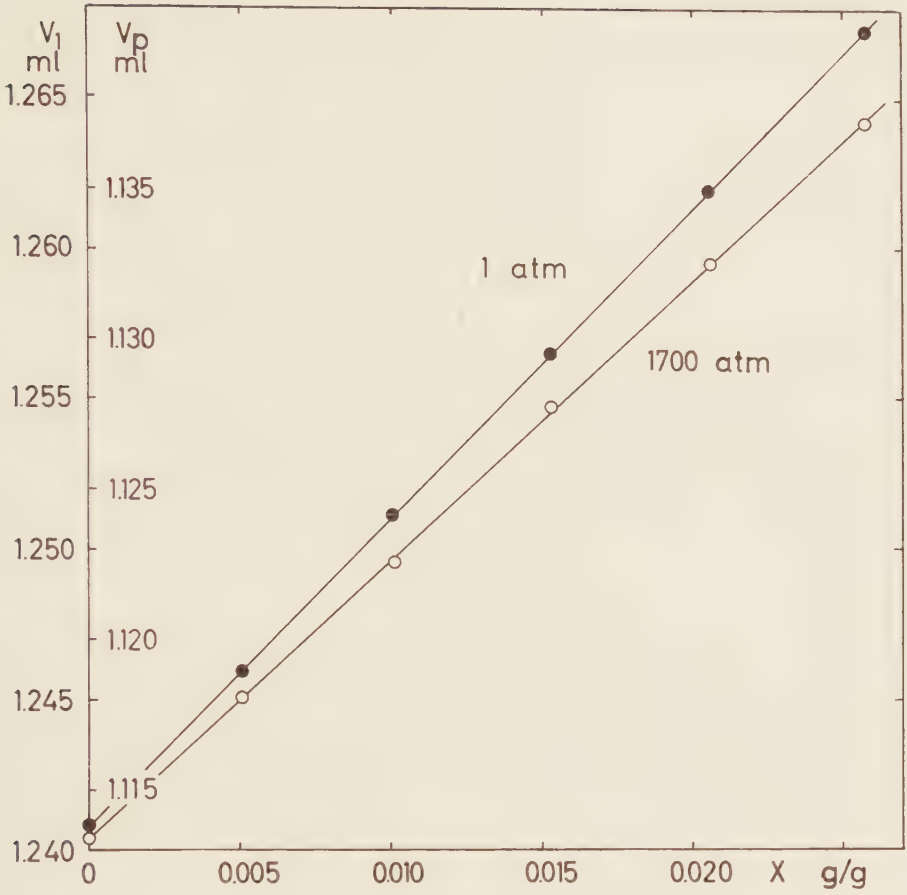

Fig. 8. A plot of v_1 versus x at 1 atm (●) and v_p versus x at 1700 atm (○) for polydimethylsiloxane in methyl ethyl ketone at 20.0°C. $(\bar{v}_2)_1 = 1.0288$ ml/g, $(\bar{v}_2)_{1700} = 0.9291$ ml/g.

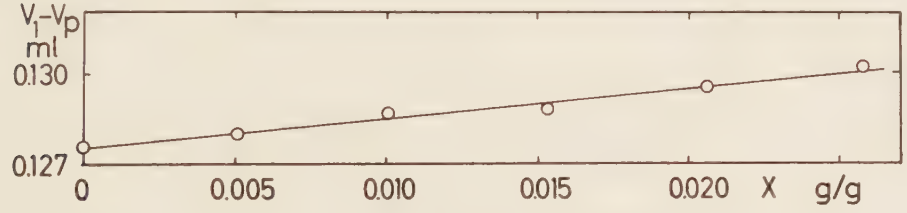

Fig. 9. A plot of $v_1 - v_p$ versus x for polydimethylsiloxane in methyl ethyl ketone at 20.0°C. $p = 1700$ atm.

$$\varrho_{x_2} = \frac{\varrho_0}{1 - x_2(1 - \bar{v}_2\varrho_0)}, \tag{20}$$

where ϱ_0 is the density of the solvent and ϱ_{x_2} that of the solution with the concentration x_2. Equation (20) permits the computation of the density of any solution from

given values of $\bar{v}_2$ and ϱ_0. As the quantity $x_2(1-\bar{v}_2\varrho_0)$ is small in the concentration ranges investigated, equation (20) can with good accuracy be written

$$\varrho_{x_2} = \varrho_0 + x_2 \cdot \varrho_0(1-\bar{v}_2\varrho_0) = \varrho_0 + E \cdot x_2. \tag{21}$$

The factor $E = \varrho_0(1-\bar{v}_2\varrho_0)$ has been computed and is tabulated for different polymer-solvent systems in the summary. The fact that the densities of the polymer solutions to a very good approximation are rectilinear functions of the concentration has been used to check the computation of $\bar{v}_2$ described above. Thus, using the least square method, E was computed from the original ϱ_{x_2}-values at different concentrations. The check then consisted in a calculation of ϱ_{x_2} for a solution at $x_2 = 0.01$ by means of both equations (20) and (21). The deviation between the results was in general as small as $\pm 1 \cdot 10^{-5}$ g/ml.

The procedure described above for calculating the partial specific volume was used both at 1 atm and at high pressures. If, however, the partial specific volume is already known at 1 atm then its change with pressure can be determined more readily using a method involving only one plot. Using the same notations as in Section 3 b, and the self-explanatory v_p, the following system of equations is obtained,

$$v_1 = (1+x)\frac{V}{M_1}, \tag{22}$$

$$v_p = (1+x)\frac{V(1-k_g) - V_{\mathrm{Hg}}(1-k_{\mathrm{Hg}}) - V_s(1-k_g)}{M_1}, \tag{23}$$

where the quantities by which $(1+x)$ is multiplied represent the specific volume of the solution at 1 atm and at p atm. A subtraction of (23) from (22) results in equation (24)

$$v_1 - v_p = (1+x)\frac{V_{\mathrm{Hg}}(1-k_{\mathrm{Hg}}) + V_s(1-k_g) + Vk_g}{M_1}. \tag{24}$$

A plot of the right hand side of (24) against x gives a straight line, the slope of which is the change in the partial specific volume due to a pressure increase of p atm.

The first method was employed throughout the investigation, although accurate determinations of $\bar{v}_2$ at 1 atm were available for some of the substances investigated. In these cases, however, the calculation of the partial specific volume from the densities of the polymer solutions, which were obtainable from the determination of the volume of the trapped mercury, provided a valuable means of controlling the reliability of the pycnometer method used. The second method was used at times to check the results obtained by the first. A volume-concentration plot at 1 atm and 1700 atm for polydimethylsiloxane in methyl ethyl ketone is shown in Fig. 8. The difference between the partial specific volumes at 1 atm and at 1700 atm is clearly demonstrated by the different slopes of the lines. In the example chosen the spreading of the data is typical of that obtained throughout the investigation. A graph based on equation (24) for the same polymer-solvent system is given in Fig. 9.

The partial specific volume was determined at 1 atm and at two elevated pressures for most of the polymers. Polystyrene, cellulose triacetate and polydimethylsiloxane were investigated more thoroughly, measurements being made at several high pres-

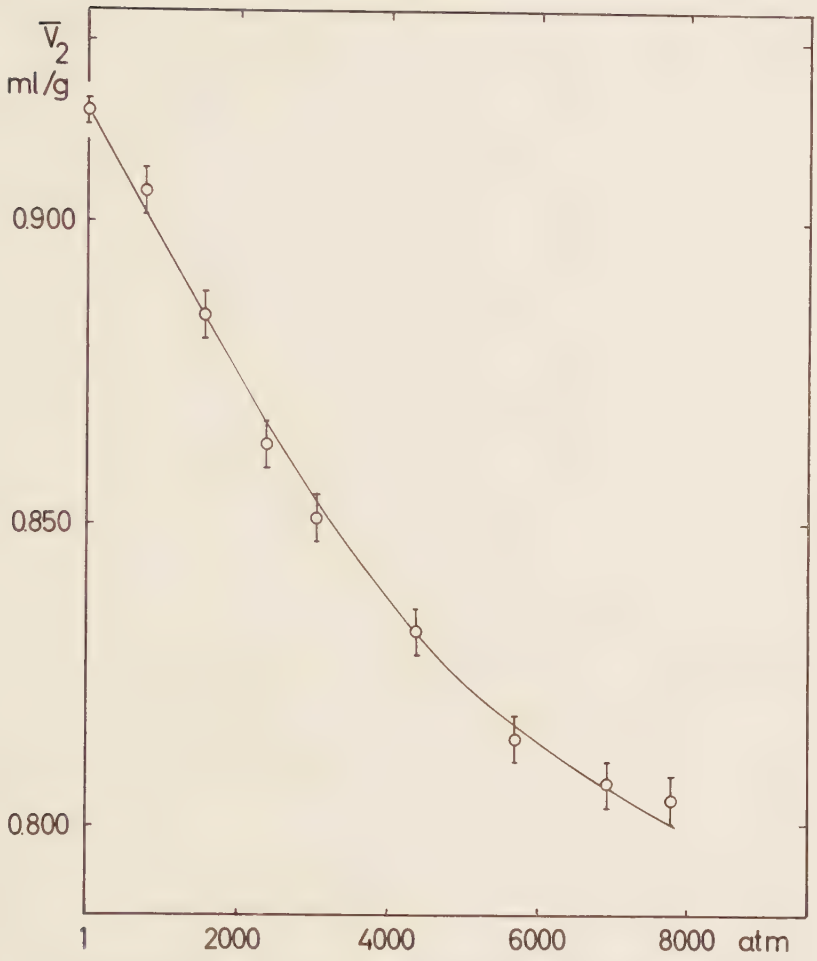

Fig. 10. The partial specific volume, $\bar{v}_2$, of polystyrene in toluene at different pressures. The given standard deviations are averages for polystyrene at 1 atm and at high pressures. Temperature 22.7°C.

sures. For some of the polymers two determinations were made at the same high pressure to check the reproducibility of the measurements.

As would be expected, the partial specific volume of polymers decreases with increasing pressure, except for polyelectrolytes. The decrease is generally small for the investigated substances and amounts to between 0.00 ml/g and 0.08 ml/g when the pressure is increased from atmospheric pressure to 1000 atm. An inspection of Fig. 10 reveals that $\bar{v}_2$ decreases almost proportionally with pressure in the lower pressure regions up to about 3000 atm, and then less rapidly. A similar change of $\bar{v}_2$ was also obtained for the partial specific volume of cellulose triacetate. For these two substances, polynomials of different degrees were tried to express $\bar{v}_2$ as a function of the pressure. Within the limits of accuracy of the data a second degree polynomial

Table 16. Experimental values of $\bar{v}_2$ and values calculated according to Eq. (25) for polystyrene at 22.7°C and cellulose triacetate at 21.9°C.

Substance and solvent	Pressure atm	$\bar{v}_2$ ml/g Observed	$\bar{v}_2$ ml/g Calculated	Observed–Calculated	Eq. (25)
Cellulose triacetate in *sym*-Tetrachloroethane	1	0.7439	0.7439	0.0000	$\bar{v}_2 = 0.7439$
	1404	0.7191	0.7188	0.0003	$-1.98 \cdot 10^{-5} p$
	2685	0.6996	0.7005	−0.0009	$+1.35 \cdot 10^{-9} p^2$
	4422	0.6840	0.6827	0.0013	
Polystyrene in toluene	1	0.9183	0.9183	0.0000	$\bar{v}_2 = 0.9183$
	759	0.9050	0.8991	0.0059	$-2.64 \cdot 10^{-5} p$
	1540	0.8844	0.8812	0.0032	$+1.50 \cdot 10^{-9} p^2$
	2359	0.8632	0.8644	−0.0012	
	3053	0.8511	0.8517	−0.0006	
	4357	0.8321	0.8318	0.0003	
	5677	0.8142	0.8168	−0.0026	
	6896	0.8065	0.8076	−0.0011	
	7756	0.8041	0.8038	0.0003	

$$\bar{v}_2 = a_0 + a_1 p + a_2 p^2 \tag{25}$$

proved to be satisfactory, as is demonstrated in Table 16.

c. *Work of compression of the partial specific volume*

The work done in compressing the partial specific volume, defined as

$$W = -\int_1^p p \left(\frac{\partial \bar{v}_2}{\partial p}\right) dp, \tag{26}$$

was computed by graphical integration for cellulose triacetate up to 4500 atm and for polystyrene up to 8000 atm (Fig. 11). The values for the work, calculated by integration of (26) using the polynomials given in Table 16, are in good agreement with the values for the work obtained graphically, except at pressures above 7000 atm. It should be noted, however, that at these pressures the magnitude of the work is very dependent on the manner in which the curve in Fig. 10 is drawn. The smaller pressure-dependence of the partial specific volume of cellulose triacetate is clearly shown in Fig. 11. Though a comparison between the partial specific volume and the specific volume can sometimes be misleading, it may nevertheless be mentioned that the work done in compressing the specific volume of water [46] and of rubber [76] is of the same order of magnitude as that for cellulose triacetate and polystyrene, at the same pressure. It is noteworthy that the curves which represent the work of compression at different pressures are also similar.

d. *Compression and compressibility of the partial specific volume*

The compression, $\bar{k}$, of the partial specific volume is defined by the equation

$$\bar{k} = -\frac{(\bar{v}_2)_p - (\bar{v}_2)_1}{(\bar{v}_2)_1}, \tag{27}$$

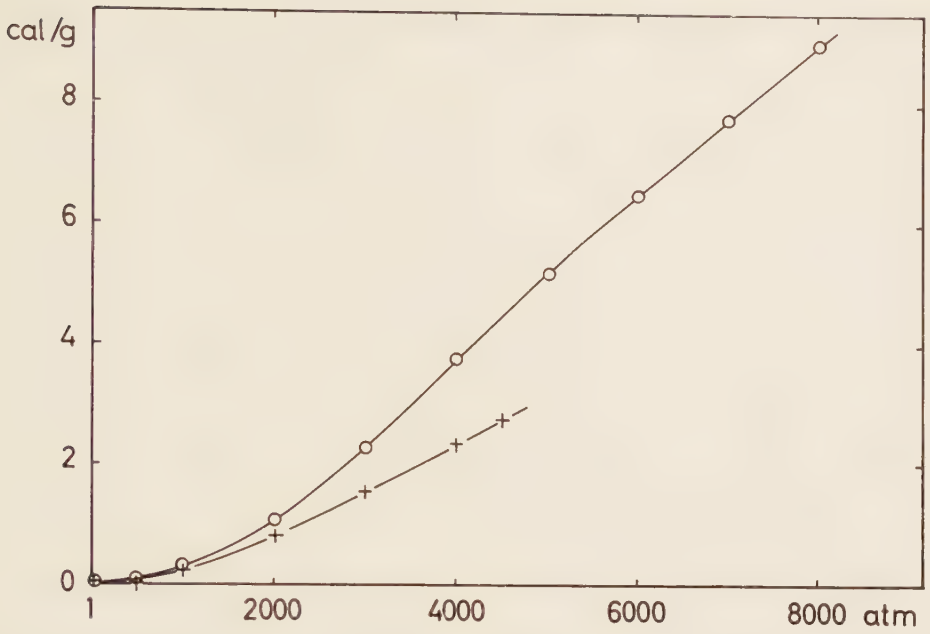

Fig. 11. The work of compression of $\bar{v}_2$ for cellulose triacetate (+) and polystyrene (○).

where $(\bar{v}_2)_1$ and $(\bar{v}_2)_p$ denote the partial specific volume of the solute at 1 atm and at p atm. The coefficient of compressibility of $\bar{v}_2$, $\bar{\beta}$, is defined analogously to the compressibility in (10) by the following equation

$$\bar{\beta} = -\frac{1}{(\bar{v}_2)_1}\left(\frac{\partial \bar{v}_2}{\partial p}\right)_T; \tag{28}$$

$\bar{\beta}$ is called the partial specific compressibility.

It follows from (27) that $(\bar{v}_2)_p = (\bar{v}_2)_1(1-\bar{k})$. A comparison with (25) shows that $a_0 = (\bar{v}_2)_1$ and that $\bar{k}$ is a function of the pressure. Following the usual convention in expressing P–V-data for liquids, $\bar{k}$ rather than $\bar{v}_2$ has been expressed as a function of p. The partial specific compressibility is then obtained as $\bar{\beta} = d\bar{k}/dp$. Because of the relatively good agreement shown in Table 16 between equation (25) and experimental data, a presentation of $\bar{v}_2$ and hence $\bar{k}$ as a second degree polynomial seems adequate:

$$\bar{k} = bp + cp^2. \tag{29}$$

In some cases the narrowness of the pressure range investigated, or an unusual spreading of the experimental data, made a rectilinear presentation more effective. For the treatment of data on the silicon polymers, the second degree polynomial representation was inadequate. Here the Tait equation was found to give a good approximation to the experimental results. The compression of $\bar{v}_2$ as a function of the pressure for cellulose triacetate and polydimethylsiloxane is shown in Fig. 12. The former substance shows an average compression of the partial specific volume, whereas the latter has a very large compression.

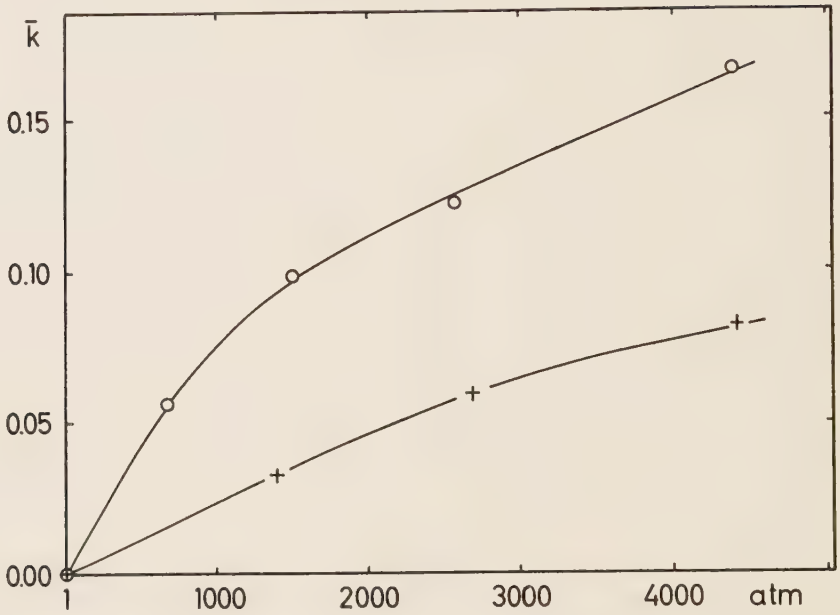

Fig. 12. The compression of $\bar{v}_2$ for polydimethylsiloxane (○) in toluene at 22.4°C and cellulose triacetate (+) in *sym*-tetrachloroethane at 21.9°C as a function of the pressure.

e. *Experimental errors in the measurements of the partial specific volume and its compression*

The standard deviation was calculated for all values of the partial specific volume. It varied considerably with the experimental conditions, such as the concentration range of the polymer solutions and the pressure at which the measurements were performed. For example, in the case of polystyrene the standard deviation varied between ± 0.0020 ml/g and ± 0.0058 ml/g in eight experiments at different pressures. For such substances as sodium carboxymethyl cellulose and nitrocellulose, which were investigated at very low concentrations (<0.8 %) and in narrow concentration ranges, the calculated standard deviation was ± 0.020 ml/g at high pressures. As a rule the standard deviation was smaller at 1 atm than at the higher pressures. The average of all the standard deviations, more than one hundred in number, was ± 0.0031 ml/g at 1 atm and ± 0.0055 ml/g at the high pressure experiments. Using these results the error in $\bar{k}$ was determined, giving a value of ± 0.008. On the basis of this the error in b in equation (29) is estimated to $\pm 0.2 \cdot 10^{-5}$ atm^{-1}, but it will be seen below that it is much smaller in many cases. Although the standard deviation affects the third decimal place in the value of the partial specific volume, $\bar{v}_2$ has been given to four decimal places in order not to introduce any rounding-off errors in the computation of $\bar{k}$.

The standard deviation of the volume measurements was obtained in a way corresponding to that for the $\bar{v}_2$-determinations. At 1 atm and at high pressures the standard deviations were $\pm 4 \cdot 10^{-5}$ ml/g and $\pm 7 \cdot 10^{-5}$ ml/g respectively.

Chapter 6. Results of the determination of the partial specific volume and its compression. Discussion of the results

a. *Glucose, dextran and cellulose derivatives*

Glucose. A Merck product of C.P. grade was used. Its moisture content was determined by drying it over phosphorus pentoxide in a desiccator.

Dextran. A fraction of the polymer, designated FDR 172, was obtained from Aktiebolaget Pharmacia, Uppsala, Sweden.

Hydroxyethyl cellulose. Cellosize WP 4400, manufactured by the Union Carbide Chemicals Company, U.S.A., was dissolved in water by shaking vigorously at +5°C. Undissolved particles were removed by centrifugation in a Spinco preparative centrifuge at 25,000 r.p.m. (55,000 *g*) for one hour. For further details about this particular sample a paper by Brown [77] can be consulted.

Sodium carboxymethyl cellulose. It is well known that it is difficult to remove interfering gel particles from water solutions of sodium carboxymethyl cellulose. A large quantity of the stock solution was therefore centrifuged at 3000 r.p.m. (3500 *g*) for several hours. The part containing a high concentration of gel particles, which was about one fourth of the whole solution, was removed and the rest was then centrifuged at 25,000 r.p.m. (55,000 *g*) for three hours. The high viscosity of the solutions prevented experiments being made at higher concentrations than about 0.4 %. The degree of substitution (D.S.) was 0.78.[1] The author is much indebted to Dr. D. Henley of this Institute for carrying out the molecular weight determination of sodium carboxymethyl cellulose; in this determination the gradient dependence of the viscosity was also taken into account. The substance designated CMC 70 high was manufactured by the Hercules Powder Company, Wilmington, Del., U.S.A.

Cellulose acetate co-butyrate, cellulose triacetate and ethyl cellulose were obtained from Polymer Consultants Ltd., Colchester, England.

Nitrocellulose was kindly placed at our disposal by Dr. P. H. Norberg of this Institute. The substance had been prepared by nitration of a sulphite pulp (Modocell from Mo och Domsjö Aktiebolag, Örnsköldsvik, Sweden). The nitrogen content of the sample, 13.66 %, was determined by the Department of Analytical Chemistry, University of Uppsala, Uppsala, Sweden. As the weighing of dry nitrocellulose in humid air is complicated by its moisture absorption, the substance was first allowed to reach equilibrium with atmospheric humidity before the stock solution was prepared. The water content of nitrocellulose at different degrees of humidity had already been determined by Dr. Arthur Bengtsson.[2] His results, which he kindly placed at our disposal, made possible the corrections necessary for obtaining the true concentration of the stock solution.

The results of the determination of the coefficients of equation (29) are presented in Table 17. When only one *b*- or *c*-value is given, as for instance in the case of cellulose triacetate and ethyl cellulose, these values have been calculated from the results of two or more experiments. In this calculation the method of least squares was used when more than two $\bar{k}$-values were available. The compression of $\bar{v}_2$ at different pressures for cellulose triacetate is shown in Fig. 12.

Among the substances in Table 17, sodium carboxymethyl cellulose is particularly noticeable in that its partial specific volume increases slightly with pressure. This

[1] The determination of the D.S. was carried out by Forskningslaboratoriet, Svenska Cellulosa Aktiebolaget, Sundsvall, Sweden.

[2] *Present address:* Department of Analytical Chemistry, University of Uppsala, Uppsala, Sweden.

Table 17. Values of b and c in Eq. (29) for glucose, dextran and different cellulose derivatives.

The partial specific volume at 1 atm, $\bar{v}_2$, is also given for each experiment.

Substance	Molecular weight	Solvent	Temperature °C	$\bar{v}_2$ at 1 atm ml/g	Pressure atm	$b \cdot 10^5$ atm^{-1}	$-c \cdot 10^9$ atm^{-2}
Glucose	180	Water	21.3	0.6201	4800	0.02	
			20.7	0.6195	4800	0.04	
Dextran	160,000	Water	20.7	0.6000	2400	0.08	
			21.9	0.6004	4800	0.27	
			20.0	0.5998	4800	0.33	
Hydroxyethyl cellulose	470,000	Water	18.9	0.6730	4800	1.07	
			19.4	0.6830	4900	1.03	
Sodium carboxymethyl cellulose	700,000	0.01 *M* NaOH	20.1	0.5040	4800	−0.96	
			21.1	0.5056	4800	−0.75	
Cellulose acetate co-butyrate	97,000	*sym*-Tetrachloroethane	22.3	0.7766	2674	2.48	1.22
			23.0	0.7777	4532		
Cellulose triacetate	250,000	*sym*-Tetrachloroethane	22.2	0.7433	1404		
			22.0	0.7436	2686	2.66	1.82
			21.5	0.7448	4422		
Ethyl cellulose	190,000	*sym*-Tetrachloroethane	21.6	0.8637	2620	2.88	1.34
			22.1	0.8647	4490		
Nitrocellulose	350,000	Ethyl acetate	20.9	0.5583	4600	0.43	
			21.7	0.5544	4600	0.42	

effect is that generally observed for electrolytes. For sodium chloride, an explanation of the effect as well as an estimation of its magnitude has been given by Hamann [78].

Assuming that the partial specific volume of a single ion in a solution of sodium chloride can be regarded as the sum of the volume of the ion itself and the change in the volume when the ion is dissolved in an infinite amount of solvent, Hamann has found that the increase of $\bar{v}_2$ with pressure is due to an increase of the solvation term. The change with pressure, which Hamann has calculated for the solvation term, is in good agreement with the increase of $\bar{v}_2$ found experimentally by Adams. The decrease in volume of the ion itself with the pressure is of little importance here, since it is small compared with the pressure increase of the solvation term. The increase of $\bar{v}_2$ for sodium carboxymethyl cellulose in Table 17 and for sodium polymethacrylate in Table 18 can probably be explained in the same way. At present, however, there do not seem to be enough experimental data in the literature on these two substances to verify this assumption.

By analogy with Harned and Owen's treatment of electrolytes [79], and to permit a further elucidation of the pressure dependence of $\bar{v}_2$ for the substances in Table 17 and the other substances covered by the present investigation, equation (13) is given in the form

$$\bar{v}_2 = \frac{V\left(1 - m_1 \frac{v^0}{V}\right)}{m_2}. \tag{30}$$

This is possible, when $\bar{v}_2$ is independent of the concentration and consequently $\varphi_2 = \bar{v}_2$ (cf. equation (19)).

The change experienced by $\bar{v}_2$ at high pressures is thus related to the pressure-dependence of the total volume of the solution, V, and the specific volume of the solvent, v^0. Both these quantities decrease with the pressure, but at different rates. For the substances in Table 17 the compression of V is less than that of v^0, and this results in an increase of $(1 - m_1 v^0/V)$. A steady decrease in V occurring simultaneously can therefore lead either to a net increase or decrease in $\bar{v}_2$; in the limiting case, there is no effect at all when the two factors exactly balance each other. The same reasoning is applicable to all the substances investigated except the two polysiloxanes. As pointed out before, toluene solutions of these two substances have a higher compression than the pure solvent, with the consequence that $(1 - m_1 v^0/V)$ will also decrease with the pressure, and $\bar{v}_2$ will increase still further.

Of the substances in Table 17, all except sodium carboxymethyl cellulose have so little influence on the compression of the solvent that the factor V exceeds $(1 - m_1 v^0/V)$, resulting in a decrease of $\bar{v}_2$ with pressure. The varying effects of the substances in Table 17 on the compression of the solvent at 4500 atm are shown in Tables 11, 12 and 15. Among the water soluble substances in Table 17, it should be noted that the partial specific volume of glucose is practically independent of pressure. For the water soluble substances, therefore, a decrease or an increase in the partial specific volume occurring with pressure depends on the magnitude of their $\partial k/\partial x_2$-values relative to that of glucose.

The reproducibility of the results in Table 17 is in most cases much better than the estimated error of b, which is $\pm 0.2 \cdot 10^{-5}$ atm^{-1}. Only sodium carboxymethyl cellulose exhibits such a high deviation between two experiments. As mentioned earlier, however, this substance had to be investigated within a very narrow concentration range, which would naturally affect the accuracy of the results.

The agreement between the partial specific volume at 1 atm found by the author and values quoted in the literature is generally good, and in some cases it is so good that the literature values fall within the limits of the experimental errors. Although the partial specific volumes have been determined at slightly different temperatures they can be compared. Thus, the investigations of Schulz and Hoffmann [80], Spencer and Gilmore [81], Griffel *et al.* [82] and Schmitt [83] show that a temperature difference of one or two degrees has a negligible effect on the partial specific volume. Gibson [84] has earlier shown that this is also true for the apparent specific volume of some electrolytes. In the following comparison the dimensions of the partial specific volume have been omitted, since in some of the papers it is not clear whether this should be expressed as ml/g or cm^3/g. In any case the dimensions have no influence on the numerical values given.

For dextran in 0.875 % NaCl, Scholz [85] has given the value 0.6003. Granath [19] has published the values 0.611 and 0.603 for two different dextran fractions in a phosphate buffer. Ingelman and Halling [86] obtained the value 0.62 again using a phosphate buffer. For sodium carboxymethyl cellulose, no $\bar{v}_2$-values seem to have been published for solutions with very high pH-values, but the value 0.509 obtained for the same substance in a water solution by Inagaki and Teramoto [87] could be mentioned for comparison. Brown [77] has obtained a somewhat higher $\bar{v}_2$-value (0.701) for hydroxyethyl cellulose in water than that given in Table 17. The $\bar{v}_2$-values for nitrocellulose in ethyl acetate agree fairly well with the value of 0.545 quoted in a paper by Newman *et al.* [88]. When the solvent is changed to acetone or *n*-butyl acetate,

Table 18. Values of b in Eq. (29) and the partial specific volume at 1 atm. $\bar{v}_2$. for polymethacrylic acid and sodium polymethacrylate.

Substance	Molecular weight	Solvent	Temperature °C	$\bar{v}_2$ at 1 atm ml/g	Pressure atm	$b \cdot 10^5$ atm^{-1}
Polymethacrylic acid	62,000	0.01 *M* HCl pH 2.0	21.0	0.7117	4900	0.97
			21.6	0.7128	4900	0.91
Sodium polymethacrylate	78,000	0.01 *M* NaOH pH 12.0	21.7	0.3842	4800	−6.46
			21.1	0.3850	4800	−6.50
Sodium polymethacrylate	78,000	0.01 *M* NaOH + 1 *M* NaCl pH 12.0	21.4	0.4153	4800	−4.41
			22.1	0.4153	4800	−4.88

$\bar{v}_2$ experiences only small changes, as is shown by the investigations of Jullander [89] and Meyerhoff [90]. No $\bar{v}_2$-values seem to have been published for the cellulose derivatives dissolved in *sym*-tetrachloroethane. Holmes and Smith [91], however, have found the value 0.70 for cellulose acetate in acetone.

b. *Polymethacrylic acid and sodium polymethacrylate*

Polymethacrylic acid. A 5.7 % stock solution was prepared from a fraction which was kindly placed at our disposal by Aktiebolaget Bofors Nobelkrut, Bofors, Sweden. The polyacid was studied at two stages of dissociation which represent practically undissociated and almost completely dissociated acid.

The potentiometric titration curve of polymethacrylic acid can be expressed by the following equation taken from reference [92]: $pH = pK - n \log(1/\alpha - 1)$, where α is the degree of dissociation and n is a constant which has the value 2 for the acid in question. The value of pK is 7, if the concentration of the polymethacrylic acid is replaced by its activity. In preparing solutions of the almost completely dissociated acid, samples of the acid were first titrated against a 1 *M* sodium hydroxide solution to pH 11 using alizarin yellow as an indicator. At this pH, about 99 % of the acid is dissociated. Additional sodium hydroxide solution was then added until pH 12.0 was reached; this was measured with a pH-meter. The solutions at pH 2.0 in hydrochloric acid were prepared in a similar manner. The high pressure treatment of the solutions did not alter their pH-values.

The results of the determinations are given in Table 18. The increase of $\bar{v}_2$ with pressure for sodium polymethacrylate is very large. In fact Adams [1] obtained approximately the same increase for sodium chloride in a 5 % solution. The addition of sodium chloride to the solvent, however, reduced the increase quite markedly. Compared with the increase for sodium polymethacrylate, the decrease of $\bar{v}_2$ with pressure for polymethacrylic acid in 0.01 *M* HCl is not entirely unexpected, since at the low pH-value of the solution the polyacid is practically undissociated. The decrease in its partial specific volume is thus in accordance with that of undissociated substances in water solution.

Table 19. Values of the coefficients b and c in Eq. (29) for some polyvinyl esters and their partial specific volumes, $\bar{v}_2$, at 1 atm.

The polymers are dissolved in cyclohexanone.

Substance	Molecular weight or $[\eta]$	Temperature °C	$\bar{v}_2$ at 1 atm ml/g	Pressure atm	$b \cdot 10^5$ atm^{-1}	$-c \cdot 10^9$ atm^{-2}
Polyvinyl chloride	$M_v = 940{,}000$	23.5	0.7135	1573	3.22	4.82
		23.2	0.7075	2613		
Polyvinyl acetate	$M_v = 48{,}000$	24.0	0.8505	1573	3.31	1.66
		23.5	0.8474	2626		
Polyvinyl chloride co-acetate	$[\eta] = 77.2$	23.3	0.7212	1582	3.24	3.54
		23.6	0.7256	2620		
Polyvinyl chloride co-vinylidene chloride	$[\eta] = 77.4$	22.2	0.7048	1572	2.42	
		23.7	0.7013	1953		

c. *Polyvinyl esters*

Polyvinyl chloride, polyvinyl acetate, polyvinyl chloride co-acetate and polyvinyl chloride co-vinylidene chloride were obtained from Polymer Consultants Ltd., Colchester, England.

Table 19 gives the results of the measurements. The compression of $\bar{v}_2$ as a function of p for polyvinyl chloride, polyvinyl acetate and the copolymer is illustrated in Fig. 13.

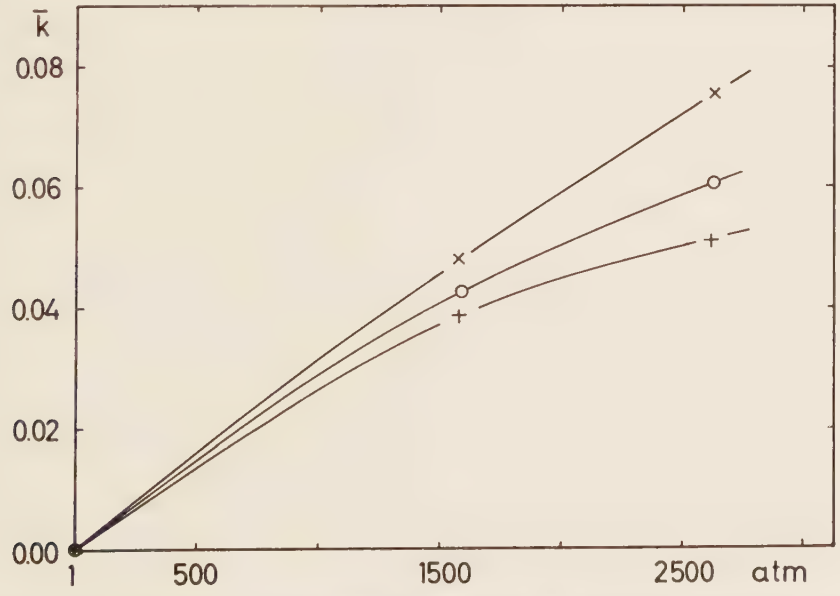

Fig. 13. The compression, $\bar{k}$, of the partial specific volume of polyvinyl acetate (×), polyvinyl chloride (+) and polyvinyl chloride co-acetate (○) as a function of the pressure.

Table 20. Values of b and c in Eq. (29) for two polyvinyl ethers and some other polyvinyl polymers and the partial specific volume, $\bar{v}_2$, of the polymers at 1 atm.

Substance	Molecular weight or $[\eta]$	Solvent	Temperature °C	$\bar{v}_2$ at 1 atm ml/g	Pressure atm	$b \cdot 10^5$ atm^{-1}	$-c \cdot 10^9$ atm^{-2}
Polyvinyl methyl ether	$M_v = 15{,}000$	*n*-Amyl alcohol	23.2	0.9832	2625	3.61	2.25
			22.7	0.9830	4514		
Polyvinyl isobutyl ether	$[\eta] = 27.7$	*n*-Amyl alcohol	19.9	1.1380	2626	5.58	5.33
			19.5	1.1369	4495		
Polyvinyl acetal	$[\eta] = 52.0$	Toluene	20.8	0.8490	2627	3.01	2.37
			20.9	0.8461	4539		
Polyvinyl butyral	$[\eta] = 122$	*n*-Amyl alcohol	20.1	0.8835	2635	2.66	1.59
			19.8	0.8823	4518		
Polyvinylcarbazole	$[\eta] = 117$	Chlorobenzene	22.9	0.7942	2588	1.67	0.33
			23.2	0.7927	4462		
Polyvinyl alcohol	$M_v = 21{,}000$	Water	21.5	0.7505	2646	0.65	
			21.6	0.7501	4536		
Polyvinylpyrrolidone	$M_v = 29{,}000$	Water	23.2	0.7813	2644	1.04	0.13
			23.0	0.7806	4509		

The self consistency of the b-values of the three first-mentioned polymers in the table and also the position of the three curves in the figure is as expected. The high chlorine content, 50.4 %,[1] of the copolymer is consistent with the small difference between the $\bar{v}_2$-values at 1 atm for polyvinyl chloride and its copolymer with the acetate, and is also reflected in their respective b-values. The $\bar{v}_2$-values for polyvinyl chloride at 1 atm compare well with the value 0.705 obtained by Oth [93], for which result cyclohexanone was again the solvent. For the polymer dissolved in tetrahydrofuran Kegeles *et al.* [94] have obtained the value 0.7429. The value 0.825 published by Elias and Patat [34], for polyvinyl acetate but dissolved in methyl ethyl ketone supports the $\bar{v}_2$-values for this polymer.

d. *Polyvinyl ethers and other vinyl polymers*

Polyvinyl methyl ether, polyvinyl isobutyl ether, polyvinyl acetal, polyvinyl butyral, polyvinylcarbazole, polyvinyl alcohol and polyvinylpyrrolidone were obtained from Polymer Consultants Ltd., Colchester, England.

The $\bar{k}$-values for the above-mentioned polymers and their $\bar{v}_2$-values at 1 atm are given in Table 20. Polyvinyl methyl ether, and more especially polyvinyl isobutyl ether, show a large pressure dependence of their partial specific volumes compared with that of the other polymers in Tables 19 and 20. The latter has in fact the most compressible partial specific volume of all the polymers investigated except for the silicon polymers. The b-values for polyvinyl acetal and polyvinyl butyral are quite close to those for the polyvinyl esters in Table 19, whereas the b-values for the two water-soluble polymers are considerably smaller.

[1] The chlorine content was determined by the Department of Analytical Chemistry, University of Uppsala, Uppsala, Sweden.

Table 21. Values given by different investigators for the partial specific volume of polyvinyl alcohol and polyvinylpyrrolidone dissolved in water.

Substance	Temperature °C	$\bar{v}_2$	Investigator	Ref.
Polyvinyl alcohol	25	0.748	Dialer *et al.*	96
		0.765	Dieu	35
	25	0.79	Martin *et al.*	98
	30	0.763	Nakanishi, Kurata	99
Polyvinylpyrrolidone		0.775	Dialer, Vogler	101
	25	0.820	Elias	102
	24.85	0.802	Miller, Hamm	103
	20	0.780	Scholtan	104
	30	0.792	Scholtan	104

To facilitate a comparison with the literature data, $\bar{v}_2$-values for polyvinyl alcohol and polyvinylpyrrolidone from several investigators have been collected in Table 21. The results of Dialer [96, 101] agree well with the findings of this investigation both for polyvinyl alcohol and polyvinylpyrrolidone. The difference between the temperatures used in the investigation of Nakanishi and Kurata and in the present investigation can account for most of the deviation in the results. The measurements of Scholtan on polyvinylpyrrolidone at 20° and 30° give some indication in this instance of the magnitude of the temperature dependence of $\bar{v}_2$.

e. *Polyacrylates and polymethacrylates*

The following polymers: polyethyl acrylate, poly-*n*-butyl acrylate, polyethyl methacrylate and poly-*n*-butyl methacrylate, were obtained from Polymer Consultants Ltd., Colchester, England. Polymethyl methacrylate was taken from the regular stock held at this Institute.

The results of a separate investigation of the pressure dependence of $\bar{v}_2$ for polymethyl methacrylate in a θ-solvent are presented in Section 6 j. The results of the $\bar{k}$-determinations for the polyacrylates and polymethacrylates in methyl isobutyl ketone are given in Table 22.

Utilizing the constants b and c in Table 22, the $\bar{k}$-values at 2500 atm were computed for the different polymers. The results were 0.077 and 0.069 respectively for polyethyl acrylate and poly-*n*-butyl acrylate; for the methacrylates the figures were 0.050, 0.058 and 0.063, taken in the same order as the polymers in the table. Assuming the same error for $\bar{k}$ as that given earlier, namely ± 0.008, it can be safely said that the partial specific volume of the two acrylates is more compressible than that of the three methacrylates. On comparing the polymethyl-, polyethyl- and poly-*n*-butyl methacrylates, taken in that order, there is a probable correlation between the increase in their partial specific volumes, the increase in the compression of the same volumes and also the increase of the formula weight of the structural unit in the formula of the polymer. The correlation does not seem to exist, however, for the acrylates, unless it is masked by exceptionally large errors for $\bar{v}_2$ and $\bar{k}$. The lack of published values for the partial specific volumes of the two acrylates makes this a difficult point to decide. For polymethyl methacrylate, however, literature data can

Table 22. Values of b and c in Eq. (29) for some polyacrylates and polymethacrylates and the partial specific volume, $\bar{v}_2$, of these polymers at 1 atm.

Solvent: methyl isobutyl ketone.

Substance	Molecular weight	Temperature °C	$\bar{v}_2$ at 1 atm ml/g	Pressure atm	$b \cdot 10^5$ atm^{-1}	$-c \cdot 10^9$ atm^{-2}
Polyethyl acrylate	34,000	24.3	0.9527	2633	3.65	2.27
		24.2	0.9486	4531		
Poly-*n*-butyl acrylate	46,000	23.3	0.9446	2623	3.24	1.88
		23.2	0.9435	4526		
Polymethyl methacrylate	480,000	21.5	0.8185	2400	2.18	0.72
		21.1	0.8119	2400		
		22.8	0.8173	4700		
		21.9	0.8146	4800		
Polyethyl methacrylate	410,000	23.0	0.8618	2617	2.60	1.08
		22.7	0.8637	4528		
Poly-*n*-butyl methacrylate	820,000	21.7	0.9206	2623	2.84	1.33
		20.7	0.9235	4482		

be quoted which agree with those in Table 22. With methyl ethyl ketone and *m*-xylene as solvents Schulz and Hoffmann [80] obtained 0.799 and 0.810 respectively at 25°C.

f. *Polyethylene glycol, polyisobutylene and nylon*

Polyethylene glycol and nylon (polyhexamethylene adipamide) were obtained from Polymer Consultants Ltd., Colchester, England. Three fractions of polyisobutylene were kindly placed at my disposal by the Esso Research and Engineering Company, Linden, N.J., U.S.A.

Two samples of polyethylene glycol, one liquid with low molecular weight and one solid with high molecular weight, were investigated. The results of the determinations of $\bar{v}_2$ and $\bar{k}$ are given in Table 23. The calculated values of $\bar{k}$ at 2500 atm for the three polyisobutylene fractions are 0.056, 0.052 and 0.058, in order of increasing molecular weight. The experimental error of ± 0.008 makes it impossible to decide from these values whether or not there is a molecular weight dependence of the compression of $\bar{v}_2$, but if any exists it must be small (cf. p. 538). The results of the experiments with polyethylene glycol are also in agreement with this statement. The $\bar{k}$-values at 2500 atm, 0.027 and 0.025 are, in this instance also, very close to each other.

The relatively large deviations between the partial specific volumes of the three polyisobutylene fractions are hard to explain. Since there is no unambiguous trend in the $\bar{v}_2$-values, and the molecular weight of the lowest fraction is relatively high, a molecular weight dependence of the type discussed, for instance, by Schulz and Hoffmann [80] and by Nakanishi and Kurata [99] cannot account for the discrepancy in the values. For polyethylene glycol, however, where one of the samples has a very low molecular weight, this molecular weight dependence, which is inversely proportional to the molecular weight, gives a more likely explanation for the deviation

Table 23. Values of b and c in Eq. (29) for polyethylene glycol, polyisobutylene and nylon and their partial specific volumes, $\bar{v}_2$, at 1 atm.

Substance	Molecular weight	Solvent	Temperature °C	$\bar{v}_2$ at 1 atm ml/g	Pressure atm	$b \cdot 10^5$ atm^{-1}	$-c \cdot 10^9$ atm^{-2}
Polyethylene glycol	240	Water	22.8	0.8452	2632	1.07	
			23.2	0.8464	4556		
Polyethylene glycol	470,000	Water	22.8	0.8330	2641	0.98	
			22.8	0.8358	4153		
Polyisobutylene	52,000	*n*-Octane	20.8	1.0730	2619	2.54	1.21
			20.9	1.0704	4517		
Polyisobutylene	1,600,000	*n*-Octane	23.4	1.0681	2620	2.41	1.34
			23.0	1.0691	4530		
Polyisobutylene	9,600,000	*n*-Octane	21.0	1.0781	2641	3.17	3.36
			20.4	1.0725	4530		
Nylon	16,000	98–100 % Formic acid	22.2	0.8900	755	1.96	
			22.5	0.8907	1061		

between the $\bar{v}_2$-values of the two samples. The partial and apparent specific volumes of polyisobutylene vary appreciably with the solvent used, according to literature data. Jessup [11] and Hort *et al.* [105] have obtained the values 1.109 and 1.105 respectively with benzene as a solvent, whereas Wales *et al.* [106] and van Holde and Williams [107] obtained 1.059 in 2,2,4-trimethylpentane (isooctane) at 25°C. The determination of $\bar{v}_2$ for nylon in formic acid had to be carried out at low pressures, because the solvent freezes at 20.6°C under 1000 atm. No value for the partial specific volume seems to have been published.

g. *Polydimethylsiloxane and polymethylphenylsiloxane*

Polydimethylsiloxane was kindly furnished by Dr. E. P. Goodings and Dr. G. W. Taylor of the Imperial Chemical Industries Ltd., Harrogate, England, and polymethylphenylsiloxane, designated MS 510/500, was obtained from Midland Silicones Ltd., London, England.

As mentioned before, the compression of $\bar{v}_2$ for the two silicon polymers is not adequately expressed by means of a second degree polynomial. This is fairly evident on comparison of the compression curves of $\bar{v}_2$ for polydimethylsiloxane and cellulose triacetate in Fig. 12. The compression of $\bar{v}_2$ for the former substance, however, can be expressed by means of the Tait equation (6). With the B- and C-values given in Table 24, the Tait equation gives compression values of $\bar{v}_2$ which are all within the limits of error of the experimentally determined $\bar{k}$-values. On comparing the two substances in Table 24, it can be seen that B varies, whereas the value of C is practically constant when changing from polydimethylsiloxane to the closely related polymethylphenylsiloxane. The constancy of C for *pure liquids*, such as benzene and some of its derivatives, is pointed out in the earlier mentioned paper by Gibson and Loeffler [51].

Table 24. The coefficients B and C of the Tait equation $\bar{k} = C \log ([B+p]/[B+1])$ for polydimethylsiloxane and polymethylphenylsiloxane and their partial specific volumes, $\bar{v}_2$, at 1 atm.

Solvent: toluene.

Substance	Molecular weight or $[\eta]$	Temperature °C	$\bar{v}_2$ at 1 atm ml/g	Pressure atm	B atm	C
Polydimethylsiloxane	$M_v = 9400$	23.2	1.0248	676	685	0.1883
		22.3	1.0242	1500		
		22.1	1.0256	2567		
		22.0	1.0222	4388		
Polymethylphenylsiloxane	$[\eta] = 132$	22.0	0.9946	1513	719	0.1893
		22.0	0.9970	4391		

The compression of the partial specific volume of the two silicon polymers is the largest found among all the investigated substances. A comparison between polyisobutylene and polydimethylsiloxane, which have the structural units

in the polymer chain, is particularly interesting. In spite of the analogy between the structures, the compression values of $\bar{v}_2$ at 1000 atm are widely different: 0.023 for polyisobutylene and 0.073 for polydimethylsiloxane. The difference is emphasized by the fact that the partial specific volumes of the polymers do not differ by more than about five per cent at 1 atm (cf. Tables 23 and 24).

Table 25. The partial specific volume, $\bar{v}_2$, of polystyrene in toluene at 1 atm and the values of b and c in Eq. (29).

$M_v = 190{,}000$.

Temperature °C	$\bar{v}_2$ at 1 atm ml/g	Pressure atm	$b \cdot 10^5$ atm^{-1}	$-c \cdot 10^9$ atm^{-2}
22.9	0.9174	759	2.88	1.63
22.8	0.9183	1540		
22.3	0.9203	2359		
22.7	0.9197	3053		
22.7	0.9180	4357		
23.1	0.9172	5677		
22.0	0.9179	6896		
23.0	0.9179	7756		

Average value of $\bar{v}_2$ is 0.9183 ml/g.

h. *Polystyrene*

The sample investigated was of the regular stock of this Institute. Benzoyl peroxide had been used as an initiator in the preparation of the polymer. The partial specific volume at different pressures is given in Table 16 and in Fig. 10. The remaining results from the investigation on polystyrene are shown in Table 25.

The compression of $\bar{v}_2$ for polystyrene, which is a vinyl polymer, is roughly the average of the compressions of the vinyl polymers listed in Table 20. It is somewhat larger, however, than that of polyvinylpyrrolidone and polyvinylcarbazole; in the formulae of these two substances ring structures are also attached to the polymer chain.

As polystyrene is one of the most investigated polymers much data have been published on the partial specific and apparent specific volumes at 1 atm with toluene as a solvent. In the work by Schulz and Hoffmann [80] mentioned earlier the value 0.9169 was obtained. In close agreement with this are the values 0.919 and 0.9188 obtained by Rosen [108] and Griffel *et al.* [82] respectively. In a paper by Spencer and Gilmore [81] the value 0.9134 is given, and the result 0.914 obtained by Streeter and Boyer [109] is in good agreement with this. The average value of the partial specific volume in Table 25, namely 0.9183 ml/g, is in very good agreement with the three first mentioned values. In fact, all three lie within the limits of error, ± 0.003, even when differences in the temperatures of the experiment in the various investigations are taken into account.

i. *Serum albumin*

Bovine serum albumin was obtained from the Armour Laboratories, Chicago, Ill., U.S.A. The substance was investigated in an aqueous solution, a citrate-phosphate buffer pH 4.0 and a phosphate buffer pH 6.2. The buffer solutions were prepared according to a standard procedure [110]. The nitrogen content of the albumin, 15.12 %, was determined[1] according to the Kjeldahl method on the micro scale. Using a nitrogen factor of 6.23 the results agreed to within 0.4 % with the results obtained by drying the albumin in an oven.

In albumin solutions, the highest pressure at which measurements can be carried out is not only limited by the freezing of the solvent but also by the fact that the albumin coagulates at high pressures. A determination of $\bar{v}_2$ at 4800 atm which had been planned could not therefore be carried out, but at 2900 atm, the highest pressure at which measurements were made, no coagulation took place.

The results in Table 26 show that the compression of $\bar{v}_2$ depends on the pH of the solution and is quite different on either side of the isoelectric point (pH 4.5–5.0). In fact the compression of $\bar{v}_2$ seems to be more pH-dependent than does the partial specific volume at 1 atm. The value of the partial specific volume in water is in very good agreement with the result of Dayhoff *et al.* [111], 0.734_3 ml/g, obtained in a determination using the magnetic float method. The $\bar{v}_2$-values at pH 4.0 and pH 6.2 also compare well with the results of the extensive study of the partial specific volumes of proteins by Charlwood [112].

j. *Measurements of the partial specific volume at the θ-temperature*

The concept of "ideal" temperature or θ-temperature for a polymer solution was introduced by Flory and Krigbaum [113]. According to the polymer-solvent model

[1] The determination was made by the Department of Analytical Chemistry, University of Uppsala, Uppsala, Sweden.

Table 26. Values of the coefficient b in Eq. (29) and the partial specific volume, $\bar{v}_2$, at 1 atm for bovine serum albumin in different solvents.

Molecular weight: 66,000 (see reference [100]).

Solvent	Temperature °C	$\bar{v}_2$ at 1 atm ml/g	Pressure atm	$b \cdot 10^5$ atm^{-1}
Water	20.2	0.7328	2900	1.34
Citrate-phosphate buffer pH 4.0	22.5	0.7336	2500	0.86
	21.9	0.7345	2600	0.88
Phosphate buffer pH 6.2	21.1	0.7384	2500	1.27
	20.9	0.7377	2600	1.19

employed by Flory, the excess chemical potential due to the interaction between polymer segment and solvent molecules is zero at this "ideal" temperature. The model used also implies that the θ-temperature represents the critical temperature for complete miscibility of polymer molecules of infinite molecular weight with the solvent, and this fact is used in the experimental determination of the θ-point by phase separation measurements. Another method for determining the θ-temperature, based on osmotic measurements of the deviation from ideality at different temperatures, demonstrates the analogy between the θ-temperature for a polymer solution and the Boyle temperature for a real gas.

The systems investigated were polydimethylsiloxane dissolved in methyl ethyl ketone and polymethyl methacrylate in *m*-xylene. The θ-temperature for the first system is 20.0°C [114] and for the second, 29.5°C, the latter being obtained by means of an interpolation procedure from data given by Schulz and Doll [115].

Polydimethylsiloxane, designated MS 200/350, was obtained from Midland Silicones Ltd., London, England.

A low molecular weight fraction of polymethyl methacrylate was prepared in the following manner: 100 g of the unfractionated polymer, obtained from this Institute, was dissolved in 2000 g *m*-xylene at +50°C. The temperature was lowered, while stirring, at a rate of about 2 degrees per hour to +15°C. During this period the high molecular weight fraction was precipitated. The supernatant liquid, containing the polymer fraction soluble in the θ-solvent at +15°C, was gently added dropwise to methanol while stirring vigorously. Addition of 200 ml of polymer solution to 1500 ml methanol during a 30 minute period was convenient to precipitate the polymer as a flocculent mass. The precipitate was rinsed with methanol and filtered through a G 2 sintered glass filter. About 25 % of the unfractionated polymer was recovered as a fraction soluble in *m*-xylene below the θ-point. The viscosity average molecular weight of the fraction prepared in this way was 190,000, whereas that of the original substance was 480,000.

At each pressure the partial specific volume was determined at the θ-temperature as well as at one temperature above it and one or two temperatures below it. In the high pressure experiments, the partial specific volumes were measured in the vicinity of 1700 atm and 3000 atm. The results of these investigations are shown in Table 27. The variation of the partial specific volume with temperature, when the pressure is held constant at 1 atm, 1700 atm and 3000 atm is given in Fig. 14.

Table 27. The partial specific volume, $\bar{v}_2$, at different temperatures and pressures of polydimethylsiloxane ($M_v = 16{,}000$) in methyl ethyl ketone and of polymethyl methacrylate ($M_v = 190{,}000$) in *m*-xylene.

Polydimethylsiloxane				Polymethyl methacrylate			
Temperature °C	$\bar{v}_2$ at 1 atm ml/g	$\bar{v}_2$ at p atm ml/g	Pressure p atm	Temperature °C	$\bar{v}_2$ at 1 atm ml/g	$\bar{v}_2$ at p atm ml/g	Pressure p atm
10.0	1.0188	0.9166	1687	17.0	0.8064	0.7659	1727
10.0	1.0172	0.8638	3011	17.0	0.8062	0.7636	2996
20.0	1.0288	0.9291	1700	22.3	0.8050	0.7756	1709
20.0	1.0276	0.8710	2965	22.0	0.8088	0.7506	2998
35.0	1.0471	0.9327	1657	29.5	0.8219	0.7715	1711
35.0	1.0455	0.8879	2932	29.5	0.8161	0.7559	2957
				45.0	0.8174	0.7656	1685
				45.0	0.8112	0.7495	2939

Inspection of Fig. 14 reveals that for polydimethylsiloxane $\bar{v}_2$ increases with temperature both at 1 atm and at higher pressures. The expansion coefficient of the partial specific volume, γ, defined as

$$\gamma = \frac{1}{\bar{v}_2} \frac{d\bar{v}_2}{dT} \tag{31}$$

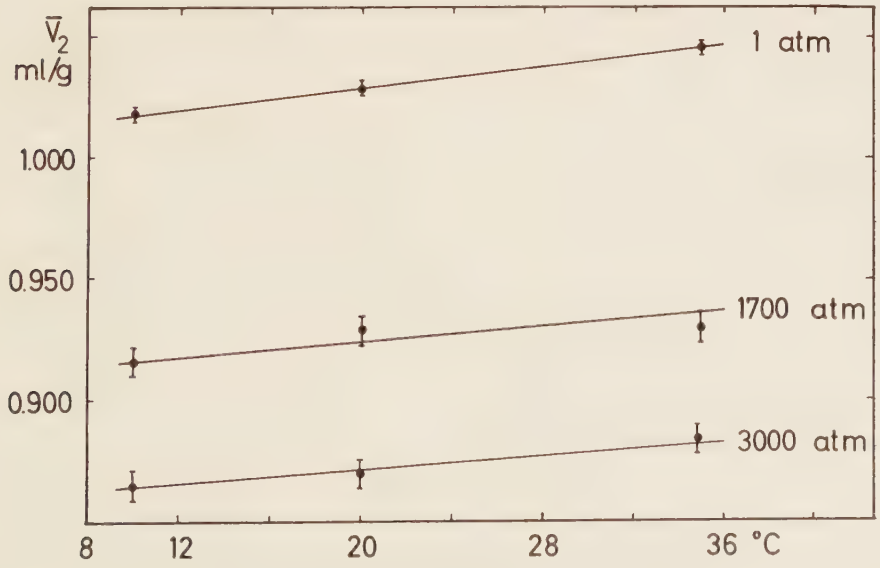

Fig. 14. The partial specific volume of polydimethylsiloxane, $\bar{v}_2$, as a function of the temperature at 1 atm, 1700 atm and 3000 atm.

Table 28. The compression of $\bar{v}_2$ for polydimethylsiloxane and polymethyl methacrylate in one good and one poor solvent.

Pressure atm	Polydimethylsiloxane		Polymethyl methacrylate	
	Toluene	Methyl ethyl ketone	Methyl isobutyl ketone	*m*-Xylene
1700	0.102	0.097	0.035	0.036
3000	0.137	0.154	0.059	0.072

was evaluated graphically at 1 atm for polydimethylsiloxane and polymethyl methacrylate. The values obtained were $11.2 \cdot 10^{-4}$ degree^{-1} and $5.2 \cdot 10^{-4}$ degree^{-1} respectively. The latter value is in good agreement with the one reported by Schulz and Hoffmann [80], $4.7 \cdot 10^{-4}$ degree^{-1}. They estimated their error to be $\pm 20\,\%$. The γ-values at 1700 atm and 3000 atm are $9 \cdot 10^{-4}$ degree^{-1} and $8 \cdot 10^{-4}$ degree^{-1} respectively, thus indicating a decrease in the expansion coefficient with pressure. In this respect the analogy can be noted with the specific volume of many liquids, where the expansion coefficient also decreases with increasing pressure. Keeping in mind, however, the larger sources of error for the determination of $\bar{v}_2$ at high pressures, the γ-values at 1700 atm and 3000 atm must be regarded as being less accurate than that at atmospheric pressure. This is also the case with the corresponding values for polymethyl methacrylate, since the partial specific volume of this substance shows a tendency to decrease with increasing temperature at high pressures. The graphically determined γ-values for this substance are $-2 \cdot 10^{-4}$ degree^{-1} and $-5 \cdot 10^{-4}$ degree^{-1} at 1700 atm and 3000 atm respectively.

The compression of the partial specific volume, $\bar{k}$, at different temperatures can be obtained from the data given in Table 27. As indicated by what has been said above, it shows a tendency to increase with temperature. At 3000 atm the $\bar{k}$-values are 0.053, 0.072, 0.075 and 0.078 for polymethyl methacrylate and 0.150, 0.154 and 0.154 for polydimethylsiloxane at the temperatures given in Table 27, taken in order of increasing temperature. At the lower pressure, 1700 atm, the trend is less regular in the $\bar{k}$-values: 0.049, 0.036, 0.061 and 0.064 for polymethyl methacrylate and 0.101, 0.097 and 0.112 for polydimethylsiloxane.

It is difficult to say whether the character of the solvent has any definite influence on the compression of $\bar{v}_2$, since each of the two polymers was investigated in one good and one poor solvent only, and the $\bar{k}$-values given in Table 28 do not show any unambiguous trend. At 3000 atm the compression of $\bar{v}_2$ in a poor solvent tends to be larger than in a good one, but this tendency does not persist at 1700 atm for polydimethylsiloxane. Table 28 was compiled from data in Tables 22, 24 and 27.

Chapter 7. General considerations concerning the compression of the partial specific volume

In order to compare the pressure effect on the partial specific volume, the $\bar{k}$-values were computed at 1000 atm for the investigated substances with the aid either of equation (29) or the Tait equation (6). In Fig. 15 these $\bar{k}$-values are plotted against the partial specific volume, $\bar{v}_2$, of the substance at 1 atm. The only substances

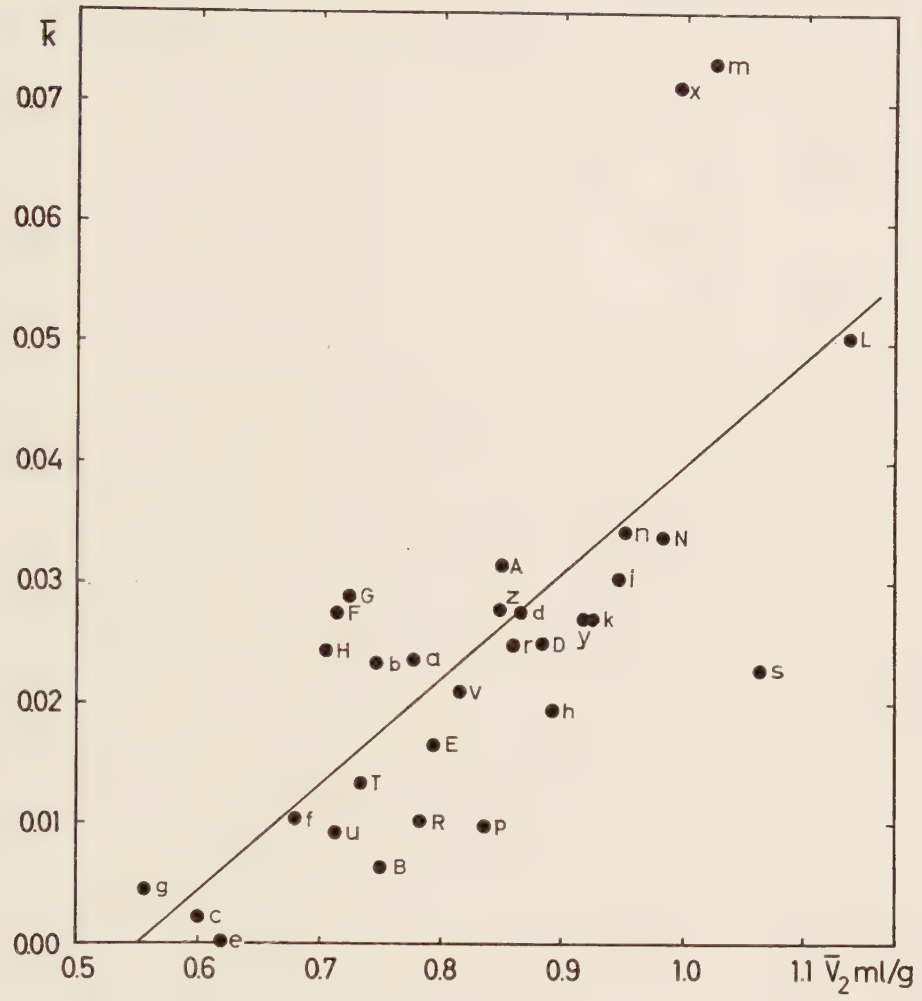

Fig. 15. The compression of the partial specific volume at 1000 atm, $\bar{k}_{1000}$, as a function of the partial specific volume at 1 atm, $\bar{v}_2$, for substances where $\bar{k} > 0$.

a = Cellulose acetate co-butyrate
b = Cellulose triacetate
c = Dextran
d = Ethyl cellulose
e = Glucose
f = Hydroxyethyl cellulose
g = Nitrocellulose
h = Nylon
i = Poly-*n*-butyl acrylate
k = Poly-*n*-butyl methacrylate
m = Polydimethylsiloxane
n = Polyethyl acrylate
p = Polyethylene glycol
r = Polyethyl methacrylate
s = Polyisobutylene
u = Polymethacrylic acid
v = Polymethyl methacrylate
x = Polymethylphenylsiloxane
y = Polystyrene
z = Polyvinyl acetal
A = Polyvinyl acetate
B = Polyvinyl alcohol
D = Polyvinyl butyral
E = Polyvinylcarbazole
F = Polyvinyl chloride
G = Polyvinyl chloride co-acetate
H = Polyvinyl chloride co-vinylidene chloride
L = Polyvinyl isobutyl ether
N = Polyvinyl methyl ether
R = Polyvinylpyrrolidone
T = Serum albumin

Table 29. The compression, k, of some polymers in the solid or amorphous state compared with the compression, $\bar{k}$, of their partial specific volumes.

ressure g/cm²	Cellulose acetate k	Cellulose triacetate $\bar{k}$	Nylon k	Nylon $\bar{k}$	Polystyrene k	Polystyrene $\bar{k}$	Polyvinyl chloride k	Polyvinyl chloride $\bar{k}$	Polydimethyl-siloxane k	Polydimethyl-siloxane $\bar{k}$	Polyvinyl alcohol k	Polyvinyl alcohol $\bar{k}$
1000	0.0201	0.024	0.0142	0.019	0.0173	0.026	0.0187	0.027	0.0742	0.072	0.0171	0.006
2500							0.0435	0.050				
5000	0.0784	0.086	0.0594		0.0724	0.101			0.1796	0.171	0.0585	0.031

not included in the figure are sodium carboxymethyl cellulose and sodium polymethacrylate, for which the partial specific volume increases with pressure.

One striking feature of Fig. 15 is that the compression values for so many of the substances lie between 0.01 and 0.03. Only the two polysiloxanes show $\bar{k}$-values which lie well outside this region. In this respect, the uniformity of the compression of the partial specific volume is similar to that of the compression of many liquids. According to the investigations of Bridgman the compression for most organic liquids lies between 0.2 and 0.3 at 12,000 kg/cm². A closer inspection of Fig. 15 reveals that there is a slight tendency for the partial specific volume to be more compressible the greater its value at 1 atm. The straight line through the assembly of points is drawn to illustrate this tendency. In drawing the line, all the $\bar{k}$-values have been given the same weight.

A comparison between $\bar{k}$, the compression of the partial specific volume of a polymer, and k, the compression of the pure polymer in the solid or amorphous state, may be of value even though no attempt is thereby made to establish a relationship between the two. For cellulose acetate [116], nylon [116], polydimethylsiloxane [64], polystyrene [116], polyvinyl alcohol [117] and polyvinyl chloride [116] compression data are available for the pure polymer and are given in Table 29 together with the compression of the partial specific volumes. As no compression values for cellulose triacetate seem to have been published, those for the acetate have been used for the sake of comparison and are assumed to be nearly the same as those for the triacetate.

Of the six different polymers in Table 29, the compressions of cellulose acetate, nylon, polystyrene and polyvinyl chloride are smaller than those of the corresponding partial specific volumes, whereas the reverse conditions exist for polydimethylsiloxane and polyvinyl alcohol. As expected, the relative differences between k and $\bar{k}$ are smaller at the higher pressures than at 1000 kg/cm². The values of k and $\bar{k}$ also show parallel variations. Thus the compressions at 1000 kg/cm² of nylon, polystyrene and polyvinyl chloride increase in this order, as do the compressions of their partial specific volumes. For polydimethylsiloxane both k and $\bar{k}$ are much larger than for the other polymers.

Since the values of k and $\bar{k}$ in the examples given do not deviate from each other by more than a factor of two or three, it may be of interest to study the effect of replacing the partial specific volume, $\bar{v}_2$, in equation (12) by the specific volume, v_2, of the polymer in the solid or amorphous state. If in addition the partial specific volume of the solvent, $\bar{v}_1$, is replaced by its specific volume v^0 and the concentrations of solvent and solute are expressed as weight fractions, x_1 and x_2 respectively, equation (12) can be written approximately

$$v \sim v^0 x_1 + v_2 x_2, \tag{32}$$

where v is the specific volume of the polymer solution. The difference $\Delta = v^0 x_1 + v_2 x_2 - v$ has been studied as a function of both concentration and pressure for polystyrene and polydimethylsiloxane dissolved in toluene. The polymers have been chosen to represent different types of $k - \bar{k}$ pairs, with respect to both the magnitude of the compression and the smallest order of magnitude whether for k or $\bar{k}$.

For polystyrene at 1 atm the difference, Δ, increases steadily with the concentration from 0.00020 ml/g to 0.00080 ml/g in the concentration range 0.005–0.025. At higher pressures the concentration dependence of Δ is more pronounced. Starting at the lowest concentration with the value 0.00037 ml/g, Δ increases to 0.00148 ml/g at the highest concentration. The figures given are averages of results from eight different experiments at 1 atm and from the same number at high pressures ranging from 759–7756 atm. The density of polystyrene, 1.054, was taken from the literature [118].

For polydimethylsiloxane the approximation introduced in equation (32) holds still better both at 1 atm and at high pressures, but the magnitude of the difference, Δ, varies rather irregularly with the concentration. However, the tendency of Δ to be larger at high pressures than at atmospheric pressure still persists. At 1 atm Δ is 0.00002 ml/g and 0.00005 ml/g in solutions with weight fractions 0.005 and 0.025 respectively. At high pressures the corresponding Δ-values are 0.00014 ml/g and 0.00017 ml/g. The density of the polymer was taken as 0.974.

In the two examples given, the error introduced by making the approximations in (32) is relatively small even at high pressures since v, v^0 and v_2 all have the order of magnitude of 1 ml/g. Before making this approximation its reliability can to some extent be estimated by studying the difference between the specific volume and the partial specific volume of the polymer at 1 atm. For polydimethylsiloxane, for which the approximation proved to be most accurate, this difference amounts to only 0.003 ml/g, whereas the corresponding difference for polystyrene is 0.031 ml/g.

Chapter 8. Corrections due to pressure effects in ultracentrifugation

As the experimental accuracy in ultracentrifugation has increased, it has been common to introduce corrections not only for the concentration dependence but also for the pressure dependence of the sedimentation coefficient. The pressure dependence is connected with the changes in viscosity and density which the investigated macromolecular solution undergoes at the high pressure (100–500 atm) developed in the cell of the ultracentrifuge. Mosimann and Signer [119] earlier put forward the equation

$$s_1 = s_p \frac{\eta_p (1 - (\bar{v}_2)_1 \varrho_1)}{\eta_1 (1 - (\bar{v}_2)_p \varrho_p)}, \tag{33}$$

which is frequently used to determine s_1, the sedimentation coefficient at 1 atm, from s_p, its value at a hydrostatic pressure of p atm, taking into account the changes with pressure in viscosity, η, density, ϱ, and partial specific volume, $\bar{v}_2$. The largest part of the pressure dependence of the sedimentation coefficient generally comes from the change in viscosity with pressure, and the pressure variation of the density. Indirectly it has been known that the pressure dependence of the partial specific

volume of macromolecules ought to be small, as molecular weights obtained by the sedimentation diffusion method are in agreement with those obtained by other methods. Early experiments at high pressures by Drucker [69] on acetic acid also gave Mosimann and Signer [119] reason to suppose that there is only a small pressure dependence for the partial specific volume of macromolecular organic substances. In practice, the variation of the partial specific volume with pressure during ultracentrifugation has therefore usually been neglected by comparison with the pressure dependence of the viscosity and the density; see for instance an investigation by Elias [120]. Cheng and Schachman [121], however, have shown that such a treatment can lead to very large experimental errors when $(1-(\bar{v}_2)_p \varrho_p)$ in equation (33) is small.

Oth and Desreux [122] have devised two extrapolation procedures to correct experimentally for the effect of the hydrostatic pressure. According to one of the methods the sedimentation coefficient is determined at constant centrifuge speed at different distances from the meniscus in the cell and is then extrapolated to the meniscus, where the pressure influence vanishes. In the other method, the centrifuge is rotated at different speeds in a series of experiments and the sedimentation coefficient at each speed is determined at the same distance from the meniscus. The sedimentation coefficient is then extrapolated to zero speed of the centrifuge, when the pressure effect is also zero. The methods of Oth and Desreux are particularly useful in cases where compressibility data for viscosity, density and partial specific volume are not available.

The influence of the pressure dependence of the partial specific volume on the sedimentation coefficient has been theoretically treated in papers by Williams *et al.* [123] and Baldwin and van Holde [124]. In a comprehensive article [125], and in a recently published monograph [126], Fujita has studied the effects of hydrostatic pressure on sedimentation in the ultracentrifuge and also theoretically treated the exprapolation procedures of Oth and Desreux. In connection with the papers of Fujita, investigations by Wales [127] and Billick [128, 129] should be mentioned.

Following the treatment of Oth and Desreux [122], equation (33) can be expressed in another form, which is convenient in making pressure corrections to the sedimentation coefficient. It is assumed that at p atm, the density, ϱ_p, the viscosity, η_p, and the partial specific volume, $(\bar{v}_2)_p$, can be expressed by the following equations,

$$\varrho_p = \varrho_1(1+\varepsilon p), \tag{34}$$

$$\eta_p = \eta_1(1+\lambda p), \tag{35}$$

$$(\bar{v}_2)_p = (\bar{v}_2)_1(1-\bar{\beta}p), \tag{36}$$

where the index 1 refers to a pressure of 1 atm. After the introduction of these relations and a few rearrangements equation (33) can be written

$$s_p = \frac{s_1\left[1-\dfrac{(\varepsilon-\bar{\beta})(\bar{v}_2)_1\varrho_1 p}{1-(\bar{v}_2)_1\varrho_1}+\dfrac{\varepsilon\bar{\beta}(\bar{v}_2)_1\varrho_1 p^2}{1-(\bar{v}_2)_1\varrho_1}\right]}{1+\lambda p} \tag{37}$$

which leads to the final expression

$$s_p = s_1(1-\mu p), \tag{38}$$

Table 30. Values at 20°C of $(\varepsilon - \bar{\beta})(\bar{v}_2)_1 \varrho_1/(1 - (\bar{v}_2)_1 \varrho_1)$, λ and μ at 1 atm and 100 atm. The relationship between these three quantities is given in Eq. (39).

Substance	Solvent	$\frac{(\varepsilon - \bar{\beta})(\bar{v}_2)_1 \varrho_1}{1 - (\bar{v}_2)_1 \varrho_1} \cdot 10^5$ atm^{-1}		$\lambda \cdot 10^5$ atm^{-1}		$\mu \cdot 10^5$ atm^{-1}	
		at 1 atm	at 100 atm	at 1 atm	at 100 atm	at 1 atm	at 100 atm
Polyvinyl butyral	*n*-Amyl alcohol	16.3	15.1	104.6	107.3	120.9	122.4
Polyvinyl isobutyl ether	*n*-Amyl alcohol	43.4	38.5	104.6	107.3	148.0	145.8
Polyvinyl methyl ether	*n*-Amyl alcohol	21.6	19.8	104.6	107.3	126.2	127.1
Polyvinylcarbazole	Chlorobenzene	41.5	36.4	41.6	62.9	83.1	99.3
Nitrocellulose	Ethyl acetate	11.1	7.7	69.2	73.7	80.3	81.4
Polyisobutylene	*n*-Octane	27.4	23.6	181.0	145.0	208.4	168.6
Polydimethylsiloxane	Toluene	−22.4	−23.1	73.7	77.2	51.3	54.1
Polymethylphenylsiloxane	Toluene	−14.6	−16.0	73.7	77.2	59.1	61.2
Polystyrene	Toluene	24.1	18.0	73.7	77.2	97.8	95.2
Polyvinyl acetal	Toluene	16.8	12.5	73.7	77.2	90.5	89.7
Dextran	Water	6.6	6.4	−2.0	−1.5	4.6	4.9
Hydroxyethyl cellulose	Water	7.6	7.3	−2.0	−1.5	5.6	5.8
Polyethylene glycol	Water	19.8	19.1	−2.0	−1.5	17.8	17.6
Polyvinyl alcohol	Water	11.9	11.5	−2.0	−1.5	9.9	10.0
Polyvinylpyrrolidone	Water	12.7	12.3	−2.0	−1.5	10.7	10.8
Serum albumin	Water	9.1	8.7	−2.0	−1.5	7.1	7.2
Sodium carboxymethyl cellulose	0.01 *M* NaOH[a]	5.6	5.4	−2.0	−1.5	3.6	3.9
Sodium polymethacrylate	0.01 *M* NaOH[a]	7.0	6.8	−2.0	−1.5	5.0	5.3
Polymethyl methacrylate	*m*-Xylene	14.3	13.2	116.6	92.0	130.9	105.2

[a] In the computation of μ, the ε- and λ-values for water were used.

where

$$\mu = \lambda + \frac{(\varepsilon - \bar{\beta})(\bar{v}_2)_1 \varrho_1}{1 - (\bar{v}_2)_1 \varrho_1}. \tag{39}$$

In Table 30 the pressure coefficient, μ, of the sedimentation coefficient is given for some combinations of polymer and solvent for which values of $\bar{\beta}$, ε and λ are available.

Bridgman's determinations [130] at 30° and 75° of η_p/η_1 at different pressures have been the basis for the computation of λ at 20°C and at the pressures 1 atm and 100 atm. At each temperature the best seventh degree polynomial was fitted to Bridgman's data, using the digital computer for the calculation of the polynomial coefficients. With the aid of the polynomials, λ was computed at 30°C and 75°C from which the λ-value at 20°C was obtained by linear extrapolation. For water, λ was computed from Bridgman's measurements at 10.3°C and 30°C. Except in the case of *n*-octane the agreement is good between the λ-values at 30°C obtained in the manner described and those given by Baldwin and van Holde [124] which are also based on the investigation by Bridgman [130].

Although the coefficient ε defined by equation (34) is not identical with the compressibility of the solvent, negligible errors are introduced by replacing ε by the compressibility. The compressibilities at 1 atm and 20°C of chlorobenzene, ethyl acetate, toluene, water and *m*-xylene were taken from Tyrer [61], that of *n*-amyl alcohol from Landolt-Börnstein [131] and the compressibility of *n*-octane was computed from

data by Eduljee *et al.* [95]. At 100 atm the compressibility of chlorobenzene and water was computed from sources given by Gibson [52, 49], that of *n*-octane was obtained from the same reference as above for octane [95]. From data given by Bridgman [64, 97] the compressibilities of *n*-amyl alcohol, ethyl acetate and *m*-xylene were computed in a way corresponding to that described for the computation of $\bar{\lambda}$. Finally the compressibility of toluene was taken from the present investigation together with the partial compressibilities, $\bar{\beta}$, of the polymers listed in Table 30. The fact that in some cases $\bar{\beta}$ is determined at temperatures which deviate from 20°C by one or two degrees was not taken into account in the computation of μ in equation (39), since the temperature dependence of $\bar{\beta}$ is known approximately only for two of the polymers. The error which is thereby introduced is certainly less than that of $\bar{\beta}$ ($\pm 0.2 \cdot 10^{-5}$ atm^{-1}). The determination of $\bar{k}$ for polydimethylsiloxane and polymethyl methacrylate at different temperatures gives some idea of the temperature dependence of $\bar{\beta}$.

The small pressure effect on the sedimentation coefficient of macromolecules dissolved in water, which has long been known, is clearly demonstrated in Table 30. In favourable cases the pressure effect is some forty times less in an aqueous solution than in a solution of an organic solvent. This is primarily due to the fact that the $\bar{\lambda}$-value for water is negative at 20°C, so that the two terms on the right hand side of equation (39) partly cancel each other. As the $\bar{\lambda}$-value for water is still more negative at temperatures between 0° and 20°C, (at 10.3°C, for instance, $\bar{\lambda} = -8.6 \cdot 10^{-5}$ atm^{-1}) it should be possible to choose a temperature at which the value of the compressibility coefficient is zero. The magnitude of the second term on the right hand side of equation (39) is markedly dependent on the partial specific volume of the solute. For example, for sodium polymethacrylate, which has a very large negative $\bar{\beta}$-value, this term is not larger than that of the other water soluble polymers, owing to the small value of the partial specific volume for this substance.

The polymer can also exhibit a small value for the pressure coefficient, μ, when its partial specific volume shows a higher compressibility than that of the solvent. This is the case with polydimethylsiloxane and polymethylphenylsiloxane. However, in spite of this, these substances are not particularly suitable for ultracentrifugation because the value of $1 - (\bar{v}_2)_1 \varrho_1$ is only 0.1 when they are dissolved in toluene.

Literature data for μ in which the pressure dependence of the partial specific volume is also taken into account are scarce. The procedure of Oth and Desreux [122] described earlier has been employed with some modifications by Billick [129] on polystyrene dissolved in toluene. The pressure coefficients obtained are generally larger than that given in Table 30 for the same polymer-solvent system. From the original paper by Oth and Desreux [122], the value $114 \cdot 10^{-5}$ atm^{-1} can be computed for polymethyl methacrylate in acetone. The value is in agreement with those listed in Table 30 for the same polymer but with *m*-xylene as a solvent.

SUMMARY

The main purpose of this investigation was to measure the pressure dependence of the partial specific volume of macromolecules in solution. To this end, the partial specific volumes of some thirty-five different macromolecular substances were determined pycnometrically at 1 atm and at high pressures, in the range 676–7756 atm. The most relevant data are collected in Table 31. During the course of the investigation, compression data for various organic liquids were obtained (Table 4) together with the concentration dependence of the density of polymer solu-

Table 31. Average values of the partial specific volume, $\bar{v}_2$, the corresponding temperature and also the compression of the partial specific volume given as $\bar{k} = bp + cp^2$ in Eq. (29).

To a good approximation, $b \cdot 10^5$ can then be regarded as the relative decrease of the partial specific volume in per cent per 1000 atm. The concentration dependence of the density according to Eq. (21), $\varrho_{x_2} = \varrho_0 + Ex_2$, is also given, with the concentration expressed as a weight fraction.

Substance	Solvent	Temperature °C	$\bar{v}_2$ at 1 atm ml/g	$b \cdot 10^5$ atm^{-1}	$-c \cdot 10^9$ atm^{-2}	E g/ml	Table No.
Cellulose acetate co-butyrate	*sym*-Tetrachloroethane	22.7	0.777	2.48	1.22	−0.378	17
Cellulose triacetate	*sym*-Tetrachloroethane	21.9	0.744	2.66	1.82	−0.297	17
Dextran	Water	20.9	0.600	0.23		0.400	17
Ethyl cellulose	*sym*-Tetrachloroethane	21.9	0.864	2.88	1.34	−0.601	17
Glucose	Water	21.0	0.620	0.03		0.381	17
Hydroxyethyl cellulose	Water	19.2	0.678	1.05		0.323	17
Nitrocellulose	Ethyl acetate	21.3	0.556	0.43		0.449	17
Nylon	98–100 % Formic acid	22.4	0.890	1.96		−0.101	23
Poly-*n*-butyl acrylate	Methyl isobutyl ketone	23.3	0.944	3.24	1.88	0.197	22
Poly-*n*-butyl methacrylate	Methyl isobutyl ketone	21.2	0.922	2.84	1.33	0.210	22
Polydimethylsiloxane	Toluene	22.4	1.024			0.100	24
Polyethyl acrylate	Methyl isobutyl ketone	24.3	0.951	3.65	2.27	0.193	22
Polyethylene glycol							
$M_v = 240$	Water	23.0	0.846	1.07		0.156	23
$M_v = 470{,}000$	Water	22.8	0.834	0.98		0.167	23
Polyethyl methacrylate	Methyl isobutyl ketone	22.9	0.863	2.60	1.08	0.248	22
Polyisobutylene							
$M_v = 52{,}000$	*n*-Octane	20.9	1.072	2.54	1.21	0.174	23
$M_v = 1{,}600{,}000$	*n*-Octane	23.2	1.069	2.41	1.34	0.177	23
$M_v = 9{,}600{,}000$	*n*-Octane	20.7	1.075	3.17	3.36	0.172	23
Polymethacrylic acid	0.01 *M* HCl pH 2.0	21.3	0.712	0.94		0.289	18
Polymethyl methacrylate	Methyl isobutyl ketone	21.8	0.816	2.18	0.72	0.278	22
Polymethylphenylsiloxane	Toluene	22.0	0.996			0.121	24
Polystyrene	Toluene	22.7	0.918	2.88	1.63	0.178	25
Polyvinyl acetal	Toluene	20.9	0.848	3.01	2.37	0.230	20
Polyvinyl acetate	Cyclohexanone	23.8	0.849	3.31	1.66	0.180	19
Polyvinyl alcohol	Water	21.6	0.750	0.65		0.251	20
Polyvinyl butyral	*n*-Amyl alcohol	20.0	0.883	2.66	1.59	0.229	20
Polyvinylcarbazole	Chlorobenzene	23.1	0.793	1.67	0.33	0.138	20
Polyvinyl chloride	Cyclohexanone	23.4	0.711	3.22	4.82	0.310	19
Polyvinyl chloride co-acetate	Cyclohexanone	23.5	0.723	3.24	3.54	0.295	19
Polyvinyl chloride co-vinylidene chloride	Cyclohexanone	23.0	0.703	2.42		0.318	19
Polyvinyl isobutyl ether	*n*-Amyl alcohol	19.7	1.137	5.58	5.33	0.059	20
Polyvinyl methyl ether	*n*-Amyl alcohol	23.0	0.983	3.61	2.25	0.163	20
Polyvinylpyrrolidone	Water	23.1	0.781	1.04	0.13	0.220	20
Serum albumin	Water	20.2	0.733	1.34		0.268	26
Serum albumin	Citrate-phosphate buffer pH 4.0	22.2	0.734	0.87		0.263	26
Serum albumin	Phosphate buffer pH 6.2	21.0	0.738	1.23		0.258	26
Sodium carboxymethyl cellulose	0.01 *M* NaOH pH 12.0	20.6	0.505	−0.86		0.495	17
Sodium polymethacrylate	0.01 *M* NaOH pH 12.0	21.4	0.385	−6.48		0.615	18
Sodium polymethacrylate	0.01 *M* NaOH + 1 *M* NaCl pH 12.0	21.8	0.415	−4.65		0.591	18

tions (Table 31). Pressure coefficients of the sedimentation coefficient in ultracentrifugation are given in Table 30. Compression data for mercury and water obtained from the literature have been re-calculated at narrow pressure and temperature intervals with the aid of a digital computer (p. 526).

In the high pressure experiments a new type of glass piezometer was used, which was constructed so that it could also be used as a pycnometer. With the aid of this instrument the density of a solution could be determined to an accuracy of $\pm 4 \cdot 10^{-5}$ g/ml at 1 atm and to $\pm 7 \cdot 10^{-5}$ g ml at high pressures. The determination of the compression of the polymer solutions was based on the usual method of measuring the volume of mercury trapped in the piezometer when the polymer solution contracts at high pressures. A new, accurate and fast method for the determination of the volume of trapped mercury is described.

Owing to the large volume of the pressure vessel used, seven piezometers, each with a volume of approximately 25 ml and containing a series of polymer solutions, could simultaneously be subjected to high pressure. This procedure of subjecting many piezometers to an identical pressure and temperature simultaneously enabled the difference between the compressions of the solvent and the solutions to be determined with a gratifying accuracy in a concentration range of the polymer as narrow as 0–0.4 %. (Tables 7 and 8). Another advantage is the gain of time, which is made in comparison with making a series of experiments with only one piezometer and one concentration at a time. The experimental procedure adopted made it possible to determine the partial specific volume at high pressures with a standard deviation of ± 0.006 ml/g.

The molecular weight of the polymer investigated had no detectable effect on the compression of the polymer solutions, and consequently no effect on the pressure dependence of the partial specific volume.

No concentration dependence of the partial specific volume was observed in any of these studies, the highest concentration range investigated being 0–6 %. The relation between the density and the concentration, expressed as a weight fraction, could therefore be represented to a very good approximation by a straight line, the slope of which is given under E in Table 31.

The partial specific volume of two polymers dissolved in poor solvents was investigated as a function of both the temperature, in the region of the θ-temperature, and the pressure (Fig. 14 and Table 27). In these two cases the character of the solvent does not produce any pronounced influences on the pressure dependence of the partial specific volume.

The partial specific volume of most of the polymers examined decreases between 1 % and 3 % as the pressure increases from 1 atm to 1000 atm. As with the electrolytes, however, the polyelectrolytes display a negative decrease, or an increase of the partial specific volume at high pressures. For all the substances investigated the change of the partial specific volume due to a pressure increase from 1 atm to 1000 atm amounts to between -6.5 % and 7.4 %, with an estimated error of ± 0.2 % (Table 31).

Owing to the relatively small pressure dependence of the partial specific volume, an indirect method, based on the compression of water and having a moderate accuracy of one or two per cent, was employed to determine the pressure in the pressure vessel.

Compression data for mercury, glass and water, necessary for the computation of the compression of the solutions and the pressure determination were obtained from the literature. The data for mercury and water are given at intervals which are too large both as regards temperature and pressure. Consequently, in order to permit a rectilinear interpolation, compression data at pressure intervals of 100 kg cm^2 and temperature intervals of 0.5°C were computed from the literature values with the aid of a digital computer. Tables of these data, together with those for Pyrex glass in the pressure range 1–12,000 kg cm^2 and the temperature range 0°–50.0°C, covering 300 pages, are available in four copies at this Institute as is also the tape from the digital computer on which the data for mercury and water were punched.

A comparison between the compression of solid or amorphous polymers and the compression of their partial specific volumes is made in Chapter 7.

The experimentally obtained compression data for some of the solvents employed were found to fit the Tait equation with good accuracy. The two characteristic constants in this equation are presented for these solvents in Table 4.

The pressure effect on the sedimentation coefficient in ultracentrifugation, arising from the pressure dependence of the partial specific volume and the density, was computed for some twenty different polymer-solvent systems (Table 30). The total pressure effect on the sedimentation coefficient, which in addition contains the pressure dependence of viscosity, was also calculated, using high pressure data from the literature. The pressure dependence of the sedimentation coefficient is smaller by approximately a factor of ten in an aqueous solution than in any of the organic solutions investigated.

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